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ON THE ACTION OF CERTAIN ACID REAGENTS ON THE SUBSTITUTED UREAS.

[FIRST PAPER.]

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IN the course of an investigation on the isourea ethers,[1] the question arose regarding the anilido hydrogen as to its ease of replacement by, and its reactivity toward, acid reagents. Since the amount of experimental evidence concerning the action of acids and acid chlorides on the substituted ureas is relatively small, a study is being made of the behavior of these bodies toward such reagents.

With an easily replaceable hydrogen, a very interesting synthesis would be possible: namely, the direct formation of acyl thio and oxygen ureas of the general type: $\begin{matrix} RNH \\ \diagdown \\ RN \diagup CO(S). \\ \diagdown \\ COR \end{matrix}$

When, however, acyl chlorides, acid anhydrides, and acids act upon these ureas, while it seems probable in many cases that the

[1] This Journal, 21, 181.

anilido hydrogen is the first point of attack, with the intermediate formation of an acyl derivative, only under especial circumstances have these intermediate bodies been isolated when this method of preparation is used. For instance, the oxygen derivatives $\begin{matrix} RNH \\ \diagdown \\ RN \end{matrix}\!\!>\!CO$ have never been prepared directly, but only by

(1) the addition of acetanilide to phenyl isocyanate,[1]

(2) the action of acid chlorides on the isourea ethers.[2]

The corresponding sulphur body $\begin{matrix} RNH \\ \diagdown \\ RN \end{matrix}\!\!>\!CS$ has, however, been isolated in the following cases:

(1) Werner[3] heated dibenzyl thiourea and acetic anhydride to the boiling-point of the latter, and obtained acetyl dibenzyl thiourea, besides small quantities of benzyl mustard oil and benzyl acetamide, the usual products of the reaction. Werner thinks that with fatty thioureas such an acyl derivative is usually formed, but he only succeeded in isolating it in the above instance.

(2) Deninger has found that acetyl chloride and thiocarbanilide in pyridine solution give mono acetyl thiocarbanilide.[4]

(3) Recently Hugershoff,[5] by modifying the process used by Werner, and heating the mixture of thiocarbanilide and acetic anhydride only to the temperature of a boiling water bath, succeeded in isolating acetyl thiocarbanilide. A yield of 45 per cent. was obtained, the rest of the thiocarbanilide having formed mustard oil and acetanilide, the products obtained by Werner at the temperature of boiling acetic anhydride.

These acyl ureas are relatively unstable bodies, and readily dissociate above their melting-points into the corresponding cya-

[1] McCreath: *Ber. d. chem. Ges.*, 8, 1181.
[2] Dains: This Journal, 21, 182.
[3] *J. Chem. Soc.*, 50, 406.
[4] *Ber. d. chem. Ges.*, 28, 1322.
[5] *Ibid.* (1899), 3649.

nates and anilides, thus giving opportunity for secondary reactions.

While it seems extremely probable, and in a number of cases is definitely proved, that the acid chlorides and anhydrides react with the ureas with the formation of such intermediate acyl ureas, yet under the conditions of the experimental work in this paper, the temperature required to produce reaction was so high that such acyl ureas were never isolated, but only their decomposition products. This fact has given rise to some interesting results.

The work in this paper has been confined to a study of the action of acids and acid chlorides on such ureas as carbanilide and thiocarbanilide, the only exception being some experiments on the action of acetic anhydride and the above reagents on the oxygen and sulphur isourea ethers. The interaction between these reagents and the monosubstituted and acyl ureas will be discussed in a later paper.

EXPERIMENTAL.

Organic Acids and Carbanilide.—Werner[1] has shown that pure acetic acid decomposes diphenyl urea at 160°–170°, giving acetanilide, carbon dioxide, and water.

Organic Acids and Thioureas.—Cain and Cohen, while investigating the "action of acetic acid on phenyl thiocarbamide," heated absolute acetic acid and thiocarbanilide at 130°–140° for three to four hours. They simply state that diphenyl urea was one of the products.[2] This is wholly in accord with the general action of anhydrous acids at temperatures above 130°. At a lower temperature, somewhat different results are obtained. Thus 9 grams of thiocarbanilide and 20 cc. of pure acetic acid were heated in a water-bath for thirty hours. The residual solid, when filtered off and examined, proved to be thiocarbanilide, and not diphenyl urea. On distilling the acid filtrate with steam, phenyl mustard oil came over, while the distilling flask was found to contain acetanilide and a base that melted at 145°,—its picrate melted at 180°, and was, therefore, triphenyl guanidine. The picrate of pure triphenyl guanidine was found by

[1] *J. Chem. Soc.*, 59, 550.

[2] Cain and Cohen: *J. Chem. Soc.*, 59, 328.

experiment to melt at 180°, and not at 178°, as given in the literature.

Under these conditions, then, the reaction follows out the lines of the decomposition of the thiocarbanilides with aqueous hydrochloric acid, the difference centering in the fact that the products of the reaction tend to form anilides with the organic acid present,—a tendency more apparent when higher temperatures are used. In this case there is first dissociation into phenyl mustard oil and aniline; and as secondary reactions, the formation of acetanilide from the aniline and the glacial acetic acid, and also, though more slowly, from the acid and the mustard oil. This interpretation is confirmed by the fact that, while at the above temperature no carbanilide is formed when absolute acid is used, with aqueous acid diphenyl urea is produced (as shown by experiment). This, as the investigation of Werner shows, is due to the action of the aqueous acid upon the phenyl thiocarbamide. It was found by direct experiment that the final products of 75 per cent. acetic acid, and thiocarbanilide at water-bath temperature are acetanilide and diphenyl urea, although the odor shows that mustard oil is an intermediate product.

Butyric Acid and Thiocarbanilide.—2.3 grams of thiocarbanilide and 2 grams of butyric acid were heated at 140°–160° for two hours. Reaction set in with the evolution of carbon dioxide and hydrogen sulphide. From the residue, by crystallization from alcohol, there was isolated butyric anilide and diphenyl urea. Carbon oxysulphide was probably evolved, but no effort was made to detect it in the presence of hydrogen sulphide and carbon dioxide. In all of these experiments, it may be said, traces of the free amine could be detected.

Benzoic Acid and Thiourea.—Molecular quantities of benzoic acid and diphenyl thiourea, at 160°–180°, evolve hydrogen sulphide, carbon dioxide, and water. As the formation of gas ceases, the melt becomes semisolid, and on examination is found to consist of a little benzoic acid which was extracted with dilute alkali, benzanilide, and a small amount of diphenyl urea.

Diparatolyl thiourea and benzoic acid, under like conditions, gave as gaseous products carbon dioxide and hydrogen sulphide, and a residue of *p*-benztoluid *p*-carbtoluid, and a little benzoic acid.

Salicylic Acid and Diphenyl Thiourea.—A mixture of these bodies in molecular proportions, when heated, liquefied at 140°, and at 150° slowly gave carbon dioxide and hydrogen sulphide. Caustic alkali separated the melt into two portions: one soluble in alkali, the other insoluble. This latter proved to be diphenyl urea. The portion soluble in the caustic soda consisted of salicylic anilide (m. p. 133.5°) and a little salicylic acid. Besides these products traces of aniline and phenol were formed,—the latter doubtless due to a slight decomposition of the salicylic acid.

The experiments presented show that the reaction between the thioureas and organic acids of the type RCOOH, proceeds along fairly definite lines. The products to be accounted for are carbon dioxide, hydrogen sulphide, water, the anilide, mustard oil and carbanilide.

The main reaction is the one already indicated:

$$\text{I.} \quad \begin{matrix}\text{RNH}\\ \text{RNH}\end{matrix}\!\!>\!\text{CS} + \text{RCOOH} = \text{RNCS} + \text{RNH}_2.\text{RCOOH}.$$

At the temperature of the reaction the amine and the acid unite.

$$\text{II.} \quad \text{RCOOH} + \text{RNH}_2 = \text{RNHCOR} + \text{H}_2\text{O}.$$

At the same time the mustard oil is attacked.

$$\text{III.} \quad \text{RNCS} + \text{RCOOH} = \text{RNHCOR} + \text{COS}. \quad (\text{HOH} + \text{COS} = \text{CO}_2 + \text{H}_2\text{S}.)$$

Only the carbanilide remains to be accounted for. This body, it will be remembered, is produced only when high temperatures are used in the reaction between thiocarbanilide and anhydrous acids. At the water-bath temperature none was formed. Werner, who has studied the reaction between acetic acid and phenyl mustard oil, says that the decomposition occurs according to the following equation:[1]

$$2\text{RNCS} + 3\text{H}_2\text{O} = (\text{RNH})_2\text{CO} + 2\text{H}_2\text{S} + \text{CO}_2.$$

In view of this it might be said that the carbanilide is due to the water formed in the reaction and the mustard oil set free at the same time. But such a conclusion must be erroneous for the following reasons:

a. At water-bath temperature none is formed;

[1] *J. Chem. Soc.*, 59, 545.

b. Much, if not all, of the water escapes at the temperature of the reaction;

c. More carbanilide is often produced than the above equation accounts for.

A very probable hypothesis is the following: at the high temperature employed, there is more or less dissociation of the thiocarbanilide into carbodiimide and hydrogen sulphide.

The carbodiimide thereupon reacts with the organic acid as follows:[1]

$$(RN)_2C + 2RCOOH = (RNH)_2CO + (RCO)_2O.$$

Dibasic Acids and the Thioureas.—Diphenyl thiourea and oxalic acid were heated at 160°–170°. The mixture melted readily, decomposed with the evolution of gas, and then partially solidified.

The gaseous products consisted mainly of carbon dioxide and hydrogen sulphide. From the solid residue, hot alcohol extracted traces of phenyl mustard oil and a little unchanged thiourea. The insoluble portion proved to be oxanilide (m. p. 240). The main reaction, then, is as follows:

$$\begin{matrix} RNH \\ \diagdown \\ \diagup \\ RNH \end{matrix}\!\!>CS + \begin{matrix} HOCO \\ | \\ | \\ HOCO \end{matrix} = CO_2 + H_2S + \begin{matrix} CONHR \\ | \\ | \\ CONHR \end{matrix}.$$

Traces of aniline could also be detected, probably in the form of aniline oxalate. No oxanilide was discovered.

Thiocarbanilide (11 grams) and succinic acid (5 grams) require a temperature of 170° before reaction sets in. At this point, however, much carbon dioxide, hydrogen sulphide, and water are evolved. The other products consisted of small amounts of aniline and mustard oil, while the residual solid could be separated by fractional crystallization into succinanil and succinanilide.

The main results can be expressed as follows:—

$$\text{I.} \quad \begin{matrix} RNH \\ \diagdown \\ \diagup \\ RNH \end{matrix}\!\!>CS + 2\begin{matrix} CH_2COOH \\ | \\ | \\ CH_2COOH \end{matrix} = 2\begin{matrix} CH_2CO \\ | \\ | \\ CH_2CO \end{matrix}\!\!>NR + 2H_2O + H_2S.$$

[1] Dains: This Journal, 21, 157.

$$\text{II.}\quad \begin{matrix}\text{RNH}\\ \text{RNH}\end{matrix}\!\!>\!\text{CS} + \begin{matrix}\text{CH}_2\text{COOH}\\ \text{CH}_2\text{COOH}\end{matrix} = \begin{matrix}\text{CH}_2\text{CONRH}\\ \text{CH}_2\text{CONRH}\end{matrix} + \text{H}_2\text{O} + \text{CO}_2 + \text{H}_2\text{S}.$$

These reactions are almost identical with those that occur when the anhydride is used instead of the acid. For instance, Dunlap[1] has found that succinic anhydride and thiocarbanilide give succinanil, succinanilide, carbonyl sulphide, and aniline. My own experiments confirm these results and show that with the elevation of temperature, there is increase in the amount of succinanilide formed. Thus, equal molecules of di-*p*-tolyl thiourea and succinic anhydride, when heated at 160°–180°, give as gaseous products carbon dioxide, hydrogen sulphide, water, and COS. The residue consisted of *p*-tolylsuccinimid and *p*-succintoluid.

It is possible that formation of succinic anhydride precedes the interaction with the thiocarbanilide, as seems to be the case with phthalic acid.

Thiocarbanilide and phthalic acid (equal molecules) reacted at 170°, with the evolution of hydrogen sulphide and carbon dioxide.

The residue was washed with cold alcohol: this removed, as was found, phenyl mustard oil, a little aniline, and a solid melting at 125°–130° which proved to be phthalic anhydride. The main product, which was insoluble in the cold alcohol, proved to be phthalanil (m. p. 205°). The reaction proceeds as if the anhydride had been used instead of the acid. The results again are in accordance with the experiments of Dunlap[1] who found that thiocarbanilide and phthalic anhydride react at 170° with the formation of phthalanil and mustard oil.

Before this paper of Dunlap's was seen, experiment showed that *p*-tolyl thiourea and phthalic anhydride react easily and smoothly at 160° yielding COS, traces of water and hydrogen sulphide, and practically quantitative amounts of p-tolyl mustard oil and *p*-tolyl phthalanil. An excess of the acid or acid anhydride increases the yield of phthalanil and decreases that of the mustard oil, since it was found by experiment that equal mole-

[1] *Am Chem. J.*, 18, 332.

cules of phthalic anhydride and mustard oil at 160° slowly give COS and phthalanil. On the contrary phenyl mustard oil and succinic anhydride do not react at 180°, but when boiled together tar is produced and an odor of phenyl isocyanate developed.

$$\begin{matrix} RNH \\ \diagdown \\ \quad CS \\ \diagup \\ RNH \end{matrix} + \begin{matrix} \diagup COOH \\ C_6H_4 \\ \diagdown COOH \end{matrix} = \begin{matrix} \diagup CO \\ C_6H_4 \\ \diagdown CO \end{matrix} \diagdown NR + RNCS + 2H_2O.$$

Acid Chlorides and Ureas.—When acid reagents like the acid anhydrides and the acid chlorides act upon the disubstituted ureas, the anilido hydrogen seems to be the main point of attack, although the actual mechanism of the reaction, whether it be one of addition or direct replacement of the hydrogen, cannot as yet be settled experimentally. The evidence points, however, to the intermediate formation in some way of an acyl derivative.

With the oxygen ureas such a compound, $\begin{matrix} RNH \\ \diagdown \\ RN \\ \diagup \\ \quad COR \end{matrix} \!\!>CO$, can never be obtained by the direct action of the acid chloride since the acyl body decomposes at a temperature below that at which the reaction is carried out.

The equations evolved in the interaction of an acid chloride and carbanilide can be represented as follows:

$$\text{I. } (RNH)_2CO + RCOCl = RNHCONR + HCl =$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad COR$$
$$RNHCOR + RNCO + HCl.$$

Under the conditions of the experiment, the acyldialphyl urea breaks down into an anilide and isocyanate, which in turn react, giving carbon dioxide and an amidine derivative.

$$\text{II. } RNHCOR + RNCO + HCl = RNH{-}CR.HCl + CO_2.$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \diagdown\!\!\!

hydrochloric acid. After the addition of water the reaction-product was shaken out with ether. This removed acetanilide.

On treating the water solution with an alkali, a base was precipitated which, on examination, was found to be acetdiphenylamidine, m. p. 131°–132° (α-phenylimido-α-phenylamidoethane). This base can be purified by recrystallization from alcohol or by dissolving in benzene, passing in hydrogen chloride, and then extracting the pure hydrochloride with water. This removes gummy impurities that are apt to remain persistently with the base. It was further identified by its platinum salt, which melted at 210°.

Analysis of two separate preparations:

1. 0.1810 gram substance gave 0.0430 gram platinum.
2. 0.1400 gram substance gave 0.0326 gram platinum.

	Calculated for $(C_{14}H_{14}N_2)_2H_2PtCl_6$.	Found. 1.	2.
Platinum	23.47	23.75	23.30

The picrate of this base melts at 165°.

I. $(C_6H_5NH)_2CO + CH_3COCl =$
$C_6H_5NHCOCH_3 + C_6H_5NCO + HCl.$

II. $\begin{matrix} C_6H_5NH \\ \\ C_6H_5N \end{matrix}\!\!>\!\!C.CH_3.HCl + CO_2.$

Nine grams carbanilide and 5 cc. butyryl chloride were heated at 150°–170° for four hours. The tube opened with much pressure due to carbon dioxide and hydrogen chloride. The contents, which formed an oily mass filled with bubbles of gas, were dissolved in alcohol and the alcohol evaporated to remove excess of the acid chloride. The ether extract gave 0.5 gram of butyric anilide, which crystallized from ligroin in square plates.

The water solution was found to contain a base, α-diphenyl butane amidine, $C_3H_7—C\begin{matrix} \diagup\!\!\diagup NC_6H_5 \\ \diagdown NHC_6H_5 \end{matrix}$. [Diphenyl butyryl amidine.] This crystallizes from alcohol, in which it is very soluble, in fine star clumps of needles, which melt at 105°.

Analysis resulted as follows:

0.600 gram substance (Kjeldahl) required 4.9 cc. normal acid.

	Calculated for $C_{16}H_{18}N_2$.	Found.
Nitrogen	11.78	11.46

When a solution of the amidine hydrochloride and chlorplatinic acid is allowed to evaporate slowly, a red platinum salt is produced.

Analysis gave the following :

0.3780 gram salt gave 0.0832 gram platinum.

	Calculated for $C_{32}H_{38}N_2Pt.Cl_6$.	Found.
Platinum	21.98	22.01

Molecular proportions of carbanilide and benzoyl chloride were heated at 160°–170° for four hours. As before, carbon dioxide was formed. From the solid contents of the tube, benzene extracted benzanilide, m. p. 161°. The residue insoluble in benzene dissolved readily in water and proved to be the hydrochloride of a base, diphenyl benzenyl amidine, formed by the action of the phenyl isocyanate on the benzanilide.

Thus Kuhn[1] has shown that phenyl isocyanate and benzanilide react at 180°–200° to form the above amidine and carbon dioxide. The base that melted at 145° was further identified by its platinum salt. This melted at 212° and gave the following figures on analysis :

0.1892 gram substance gave 0.0382 gram platinum.

	Calculated for $C_{26}H_{24}N_4PtCl_6$.	Found.
Platinum	20.39	20.19

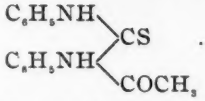
When molecular proportions of benzoyl chloride and carbanilide are heated in an open flask at 160°–200°, carbon dioxide and hydrochloric acid are given off and the intermediate formation of phenyl isocyanate is very apparent from the odor. Diphenyl benzenyl amidine was isolated as before and was identified by its own melting-point and that of its picrate (m. p. 216°).

Acyl Chlorides and Dialphyl Thioureas.—Reagents of this class act more readily on the thioureas than on the corresponding oxygen derivatives. The products of the reaction are largely dependent upon the following conditions : the presence of a solvent such as pyridine, the temperature, and the fact that the mustard oils

[1] *Ber. d. chem. Ges.*, 18, 1476.

are less reactive than the corresponding isocyanates, and so do not tend to react with the anilide formed.

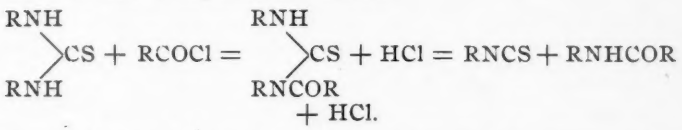
Deninger[1] has shown that by dissolving thiocarbanilide in pyridine, acyl chlorides attack the anilido hydrogen with great ease at ordinary temperatures, forming a stable substitution product. For instance, acetyl chloride and thiocarbanilide, under these conditions, give acetyl thiocarbanilide.



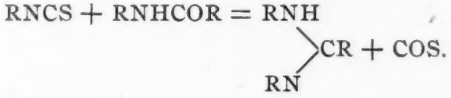
With benzoyl chloride and diphenyl thiourea, a dibenzoyl derivative was obtained. Like the oxygen bodies of similar constitution, these acyl thiocarbanilides are easily decomposed. Thus, acetyl thiocarbanilide, when heated above its melting-point or when boiled with water, gives phenyl mustard oil and acetanilide, which two components show no tendency to unite again even when heated. On the other hand, phenyl isocyanate and acetanilide heated in a sealed tube to 150° unite to form acetyl diphenyl urea.[2]

In the absence of pyridine, which combines with the hydrochloric acid set free, my experiments show that heat is required to effect complete reaction between the acyl chloride and the thioureas, and that under these conditions no intermediate product corresponding to the acyl thiocarbanilide can be isolated.

The general reaction between an acyl chloride and a dialphyl thiourea can be expressed as follows:



Mustard oil and an acyl anilide are the main products, while occasionally small quantities of an amidine base are formed.



[1] *Ber. d. chem. Ges.*, **28**, 1332.
[2] McCreath: *Ibid.*, **8**, 1181.

Acetyl Chloride and Thiocarbanilide.—Diphenyl thiourea was treated with a slight excess over 1 molecule of acetyl chloride, and, as no reaction occurred at ordinary temperatures, the mixture was warmed to 50° on the water-bath, until the evolution of hydrochloric acid ceased. The oily product, which became semisolid on cooling, was distilled with steam. Phenyl mustard oil came over. This was identified by its properties, and the formation of monophenyl thiourea. On concentrating the water solution of the residue not volatile with steam, acetanilide (m. p. 114°) was obtained. The filtrate from this, when neutralized with alkali, gave small quantities of a base which proved to be acetdiphenyl amidine, a product formed in much larger quantities in the reaction between acetyl chloride and carbanilide, and identical with the body thus obtained.

Butyryl chloride and diphenyl thiourea react with ease, giving much hydrochloric acid, and an oily product from which can be isolated phenyl mustard oil and butyric anilide. Small amounts of an impure base are also formed.

When molecular quantities of benzoyl chloride and thiocarbanilide are heated to 150°, reaction ensues with the evolution of hydrogen chloride, a little carbon dioxide, and a gas that blackens lead acetate paper. On distilling the product with steam, or by separating with cold alcohol, there can be isolated almost quantitatively phenyl mustard oil and benzanilide. Traces of the base diphenylbenzenyl amidine are also formed.

Di-*m*-xylyl thiourea and benzoyl chloride, under like conditions, react at 120°. The products were the benzoyl derivative of metaxylidine ($CH_3CH_3NH_2$1,3,4 (m. p. 192°), and xylyl mustard oil, which, with alcoholic ammonia, gave the monothiourea (m. p. 175°). Traces of an impure base were also formed.

Greater elevation of temperature does not favor this reaction between the acid chlorides and the thioureas. For instance, molecular quantities of benzoyl chloride and di-*o*-tolyl thiourea were heated in a sealed tube at 180°–200°. The tube opened with slight pressure, and the issuing gas burned with a pale blue flame. The contents of the tube consisted of *o*-tolyl mustard oil, *o*-benztoluide, much tar, and a small amount of an impure base.

Allylphenyl thiourea was warmed on the water-bath with a slight excess of acetyl chloride. The reaction-product formed a

thick oil, with the evolution of a little hydrogen chloride. On distilling this oil with steam, a few drops only of phenyl mustard oil were obtained, and the residue in the distilling flask, with the exception of a little tar, was completely soluble in water. From this, alkali threw down a base which, without further purification, melted at 115° and gave a picrate (m. p. 153°). It was, therefore, *N*-phenyl propylene pseudo thiourea. (2-Phenyl amido-5-methyl-4,5-dihydrothiazol.) This was further established by the analysis of the platinum salt.

0.6003 gram substance gave 0.1477 gram platinum.

	Calculated for $(C_{10}H_{12}N_2S)_2H_2PtCl_6$.	Found.
Platinum	24.53	24.60

The acyl chloride evidently causes a practically quantitative rearrangement. Boiling with hydrochloric acid brings about the same change.[1]

The Action of Acid Reagents on Isourea Ethers.—A study begun in a former paper on the action of acids, acid chlorides, and acid anhydrides on the isourea ethers is here continued and extended to the corresponding sulphur ethers.

Organic acids act with great ease upon the isourea ethers. Thus ethylisodi-*o*-tolyl urea and glacial acetic acid give ethyl acetate and carbanilide, as has been shown in a former paper.[2]

Towards acids and acid reagents the thio ethers show remarkable stability. Ethyl isothiocarbanilide can be boiled with glacial acetic acid without effect, the original base being recovered unchanged. When heated at 180° with acetic acid the tube opens with pressure; the issuing gases burn and form a white precipitate with a silver nitrate solution. The solid residue consists of pure acetanilide. The odor of mercaptan is apparent.

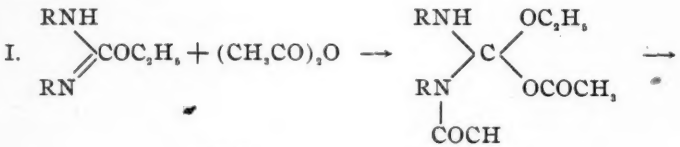
Acid of Acetic Anhydride upon the Oxygen Urea Ethers.—Ten grams of amylisodi-*o*-tolylurea and 3.5 grams of acetic anhydride were mixed. Since no apparent reaction took place after standing at ordinary temperatures, the solution was heated in an oil-bath at 150°–160° for one and one-half hours. The product, which remained oily after twelve hours' standing, was distilled at 12 mm. pressure; there was isolated amyl acetate, a

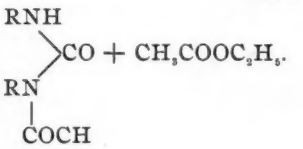
[1] Prager: *Ber. d. chem. Ges.*, **22**, 2991.
[2] This Journal, **21**, 170.

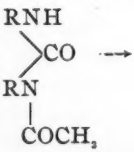
little unchanged acetic anhydride, *o*-acettoluide, and a trace of *o*-ditolylurea. The latter may be due to traces of moisture or of acetic acid in the anhydride.

Equal molecules of ethyl isocarbanilide and of acetic anhydride were heated in a test-tube fitted with an air-condenser and a calcium chloride tube for eight hours at 160°–170°. Ethyl acetate was detected by its odor. The oily product was treated with alcohol to get rid of the excess of the acetic anhydride and then recrystallized from water. Acetanilide was isolated. This same reaction was found to take place with equal ease at 130°–140°. At this latter temperature methylisocarbtoluide and acetic anhydride give methyl acetate and *o*-acettoluide. The yield of acetanilide or of *o*-acettoluide seems to be quantitative.

As in all reactions with acidic reagents there is doubtless first addition to the double bond with the formation of an unstable addition-product.





II. (*a*) 

(*b*) $RNCO + O(COCH_3)_2 \longrightarrow RN(COCH_3)_2 + CO_2$.

At the temperature of the experiments, 130°–140°, not only is this intermediate addition-product broken down, but the acetyl diphenyl urea formed is dissociated into phenyl cyanate and acetanilide: and the phenyl cyanate in turn reacts with the excess of acetic anhydride to form diacetanilide. That the diacetani-

lide was not isolated is not surprising, since it is very easily saponified.[1]

The experimental evidence for equation II is as follows:

(*a*) Acetyl diphenyl urea, when heated a little above its melting-point, dissociates, giving phenyl isocyanate and acetanilide.

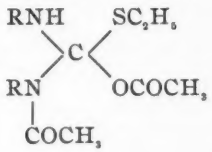
(*b*) Acetyl diphenyl urea, when heated with acetic anhydride at 130° for two hours, and the resulting product recrystallized from water, gives a quantitative yield of acetanilide.[2]

(*c*) Phenyl isocyanate and acetic anhydride give acetanilide.

In the oxygen ethers, the existence of an intermediate product due to the addition of the acid anhydride to the double bonding of the ether was assumed. With the thioethers the existence of such an addition-product was definitely proved.

Ethyl isodiphenyl thiourea and acetic anhydride can be heated to the boiling-point of the latter without seeming change, or the formation of ethyl acetate; and on careful treatment with alkali, the original base can be regenerated.

If, however, the excess of anhydride be decomposed with alcohol, the resulting oil is no longer soluble in dilute mineral acids. Alcoholic potash yields mercaptan and carbanilide, the decomposition taking place with great ease. An effort was made to purify this oil by dissolving in ether and washing with dilute sodium carbonate and water, and drying. The evaporation of the ether left a yellow oil insoluble in water and dilute alkalies. Experiment showed that alcoholic potash gave, on warming with this, mercaptan and diphenyl urea. Hence, if the body is the expected addition-product, it must decompose as follows:



$$+ 2NaOH = (RNH)_2CO + C_2H_5SH +$$

$$2CH_3COONa + H_2O.$$

The oil was analyzed by dissolving it in alcohol, adding a definite quantity of standard sodium hydroxide, boiling with a reflux

[1] Gumpert (*J. prakt. Chem.*, 31, 121), who tried the action of phenyl isocyanate and acetic anhydride, obtained only acetanilide, a result probably due to moisture.

[2] Experiments have shown that diphenyl urea and boiling acetic anhydride give acetanilide and carbon dioxide.

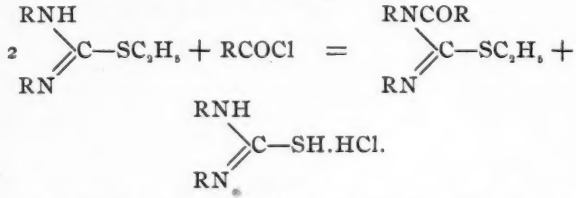
condenser until decomposition was effected, and then titrating the excess of alkali, using phenol phthalein as an indicator. The amount of acetic anhydride could thus be determined, since 1 cc. normal alkali is equal to 0.05103 gram acetic anhydride.

1. 1.7065 grams substance required 9.3 cc. alkali.
2. 1.7965 grams substance required 9.76 cc. alkali.

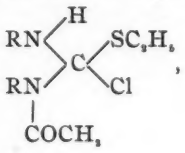
	Calculated for $C_{19}H_{22}N_2O_2S$.	Found. 1.	2.
$(CH_3CO)_2O$	28.48	27.81	27.72

The difficulty of purifying such a compound, and the ease with which it breaks down, account for the low results. At high temperatures complete reaction follows between the acetic anhydride and the ethyl isothiocarbanilide. Thus, after heating at 190°, the tube opened with pressure due to inflammable gases, while mercaptan and ethyl acetate were recognized by the odor. The solid residue in the tube was pure acetanilide.

Action of Acetyl Chloride upon Ethyl Isothiodiphenyl Urea.— Experiments in a previous paper[1] have shown that with the oxygen urea ethers, acid chlorides react, giving, by addition and subsequent decomposition, ethyl chloride and acyl diphenyl urea. With the sulphur derivatives the reaction proceeds in an entirely different manner, due doubtless to the greater stability of the thio ethers toward acid reagents, and to the more negative character of the molecule. The general reaction between the thioethers and acid chlorides is as follows:



Either the anilido hydrogen is replaced directly by the acyl group, or there is first, addition to the double bond,



[1] This Journal, 21, 181.

and then loss of hydrogen chloride, which unites with a second molecule of the urea ether to form the hydrochloride.[1]

Two molecules of the thioether were dissolved in chloroform and treated with 1 molecule of acetyl chloride. After standing for twenty-four hours, the solution was washed with water, the excess of chloroform evaporated, and the residual oil taken up with ether; this was washed again with a solution of sodium bicarbonate to remove all traces of free acid. After drying, the evaporation of the solvent left a thick oil, which could not be crystallized, and was no longer soluble in dilute acid. This was analyzed, as in the previous case, by boiling in an alcoholic solution with a standard caustic alkali, the products being sodium acetate, mercaptan, and carbanilide.

1.3554 grams substance required 4.545 cc. normal NaOH. This is equivalent to 0.1954 gram CH_3CO.

	Calculated for $C_6H_5N(COCH_3)C(=NC_6H_5)SC_2H_5$.	Found.
CH_3CO	14.42	14.41

This body, monoacetylethylisodiphenyl thiourea, is interesting as being the first acyl derivative of the isourea ethers that has been isolated. The action of this substance toward glacial acetic acid has also a direct bearing upon the mechanism of the acetic anhydride reaction described on page 195.

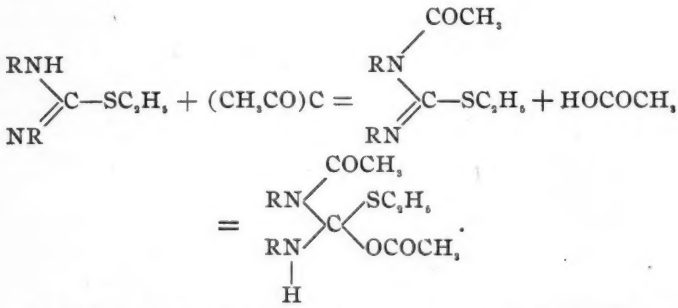
Thus, when acetyl ethyl isodiphenyl thiourea was heated to the boiling-point with an excess of glacial acetic acid and allowed to stand for twenty-four hours, the product then being poured into water and purified as in the preceding cases, the original oil was recovered, and not an acetic acid addition-product identical with the product from acetic anhydride.

0.7420 gram oil required 4.9 cc. half-normal NaOH.

	Calculated for $C_{17}H_{18}ON_2S$.	Found.
CH_3CO	14.42	14.33

This points to the conclusion that the acetic anhydride acts by direct addition to the double bond, and not by first replacing the anilido hydrogen with an acetyl group and then adding acetic acid, as follows:

[1] *Am. Chem. J.*, 19, 136.



Action of Benzoyl Chloride.—Ten grams of ethyl isodiphenyl thiourea and 3 grams of benzoyl chloride were dissolved in benzene and allowed to stand for a week. The crystals that separated weighed 5.7 grams and consisted of the pure hydrochloride of the ethyl ether (m. p. 178°). After distilling off the benzene, an oil was left, insoluble in ammonia or dilute hydrochloric acid, the benzoyl ethyl thiodiphenyl urea. It was not obtained pure enough for analysis. An effort was made to distil the oil but decomposition ensued, with the formation of much tar, some phenyl isocyanate, and carbodiphenyl imide. Another portion heated in a sealed tube with hydrochloric acid, at 140°, gave ethyl chloride, carbon dioxide, mercaptan, aniline, and benzoic acid, so that while the body was not analyzed, its identity is fairly well established.

NORTHWESTERN UNIVERSITY CHEMICAL LABORATORIES,
2421 DEARBORN ST., CHICAGO,
March, 1900.

THE TECHNICAL ESTIMATION OF ZINC.

BY ALBERT H. LOW.

Received February 26, 1900.

IN a report read June 11, 1892, before the Colorado Scientific Society, the method devised by the writer for the technical estimation of zinc in ores, etc., was approved as the best that had come to the attention of the committee. Although it had its weak points, some of which were recognized at the time, it was nevertheless well adapted for rapid and accurate work on the majority of Colorado ores and, in fact, no better method has since been offered.

Applications for a description of the method are very frequent, and in view of the fact that daily use in the laboratory for several years has naturally resulted in some changes from the original plan, it may not be out of place to again publish the scheme in its latest form. It is, of course, apparent that the method as given is not of universal application. Sometimes a fusion may be necessary to effect complete decomposition, or perhaps a preliminary treatment with hydrochloric acid may be required. (All hydrochloric acid must be expelled before beginning the regular treatment.) The operator is expected to recognize such cases and apply the remedy. He is cautioned, however, to be very careful about modifying the method except from actual necessity. Not that improvements are not possible, but it has been the writer's experience that most of the failures result either from inattention to details or the introduction of supposed improvements by the operator.

DESCRIPTION OF THE METHOD.

Standard Ferrocyanide Solution.—Dissolve 22 grams of potassium ferrocyanide crystals in water and dilute to 1 liter. Standardize as follows: Weigh carefully about 100 mg. of pure zinc and dissolve in 6 cc. of strong hydrochloric acid, using a 400 cc. beaker. Then add about 10 grams of ammonium chloride and 200 cc. of boiling water. Titrate with the ferrocyanide solution until a drop, when tested on a porcelain plate with a drop of a strong solution of uranium nitrate, shows a brown tinge. About 20 cc. of ferrocyanide will be required, and accordingly nearly this amount may be run in rapidly before making a test, and then the titration finished carefully by testing after each additional drop. Instead of using a single drop of the zinc solution for the test, the reaction is much sharper if several drops are placed in a depression of the plate and tested with a single drop of a strong uranium solution. As this is near the end of the titration the amount of zinc lost thereby is insignificant. As soon as a brown tinge is obtained, note the reading of the burette and then wait a minute or two and observe if one or more of the preceding tests do not also develop a tinge. The end-point is usually passed by a test or two and the burette reading must be accordingly corrected. A further correction must be made for

the amount of ferrocyanide required to produce a tinge under the same conditions when no zinc is present. This is only 1 or 2 drops. One cc. of the standard solution will equal about 0.005 gram of zinc, or about 1 per cent. when 0.5 gram of ore is taken for assay.

Assay of Ores.—To 0.5 gram of ore in a 250 cc. pear-shaped flask, add about 2 grams of potassium nitrate and 5 cc. of strong nitric acid. Heat until the acid is about half gone and then add 10 cc. of a cold saturated solution of potassium chlorate in strong nitric acid and boil to complete dryness. It is usually necessary to manipulate the flask in a holder over a naked flame to avoid loss by bumping. The boiling may be conducted rapidly, and towards the end it is best to heat the entire flask so as to expel every trace of liquid. The potassium nitrate serves simply as a diluent of the dry residue and insures the completeness of the subsequent extraction of the zinc. Cool sufficiently and add 30 cc. of a prepared ammoniacal solution and heat to boiling. This solution is made by dissolving 200 grams of ammonium chloride in a mixture of 500 cc. of strong ammonia water and 350 cc. of water. Boil the contents of the flask very gently for about two minutes and then filter through a 9 cm. filter and wash with a hot solution of ammonium chloride containing about 100 grams of the salt and 50 cc. of strong ammonia water to the liter. Collect the filtrate in a 400 cc. beaker. The insoluble residue should be completely disintegrated and any ferric hydroxide present should appear of a fine sandy nature. Place a bit of litmus paper in the filtrate (not necessary if much copper is present), and neutralize carefully with hydrochloric acid, finally adding 6 cc. of the strong acid in excess. Dilute to about 150 cc. and add 50 cc. of a cold saturated solution of hydrogen sulphide. Heat nearly to boiling and the solution is ready for titration. If more convenient, or apparently advisable, pass a current of hydrogen sulphide gas through the hot solution diluted to 200 cc. Copper and cadmium, which are interfering metals, are thus precipitated. Unless in large amount they need not be filtered off. Practically no zinc is precipitated with the copper under these conditions and the discoloration of the liquid by even 10 per cent. of copper does not badly mask the uranium test. Titrate the

hot solution as follows: Pour off about one-third and set it aside in a beaker. Titrate the remainder, more or less rapidly, according as much or little zinc is indicated, until the end-point is passed, using the uranium indicator as in the standardization. Now add the greater part of the reserved portion and continue the titration with more caution until the end-point is again passed. Finally add the last of the reserved portion and finish the titration carefully, ordinarily two drops at a time. Make corrections of the final reading of the burette precisely as in the standardization. The true end-point is always slightly passed, and, after waiting a minute, it is usually sufficient to deduct for as many drops as show a brown tinge and one test additional.

Notes.—When precipitating with hydrogen sulphide it is a matter of considerable importance to have the solution of a definite degree of acidity. Cadmium and copper are to be precipitated, while it is better to retain lead in solution and not unnecessarily blacken the liquid with its sulphide. If there is enough acid to prevent the precipitation of its sulphide the lead will not interfere in the titration. On the other hand too much acid will prevent the precipitation of the cadmium. It will not come down from a boiling hot solution containing 5 per cent. of strong hydrochloric acid. It is readily precipitated from a 3 per cent. solution while lead is not, if the liquid be nearly boiling. It is therefore recommended to have an excess of 6 cc. of strong hydrochloric acid in the final bulk of 200 cc. of solution.

Arsenic, when present in large amount, sometimes makes trouble by retaining iron in the ammoniacal solution. No attention need be paid to arsenic unless its presence in excess is thus indicated. In such a case begin anew and give the ore a preliminary treatment as follows:

To 0.5 gram of ore in the flask add 10 cc. of strong hydrochloric acid and 1 cc. of bromine. Warm very gently for several minutes to decompose the ore without loss of bromine and then boil rapidly to complete dryness. The arsenic will thus be sufficiently expelled. Now add the potassium nitrate and nitric acid and proceed in the usual manner.

In the case of ores that are free from cadmium, or where cadmium may be neglected, the copper may be readily precipitated without the use of hydrogen sulphide as follows: After neutral-

izing the ammoniacal filtrate from the insoluble residue, acidify with an excess of 10 cc. of hydrochloric acid and add about 30 grams of granulated test lead. Heat nearly to boiling and stir the lead about until all the copper is precipitated. Now dilute to 200 cc. and titrate as described, without removing the lead and precipitated copper.

DENVER, COLORADO, February 20, 1900.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 21.]

A NEW BRIDGE ARRANGEMENT FOR THE DETERMINATION OF ELECTROMOTIVE FORCE BY AID OF THE LIPPMANN ELECTROMETER.

BY J. LIVINGSTON R. MORGAN.

Received February 3, 1900.

THE two-bridge arrangements given by Ostwald[1] for the measurement of electromotive force by the aid of the Lippmann electrometer are the only two at present in use for primary cells. When an accumulator is used, it is only necessary to connect it through a meter of manganine wire and to compensate the cell to be measured by a fraction of the source taken off from the wire by a sliding contact.[2] If a primary cell were used in this way the results would not be accurate, owing to the decrease in the electromotive force of the cell due to the small resistance of the wire (50 ohms at most). Of the two methods in which primary cells may be used as a source, we may say that each is good for its purpose but that neither is of general utility. The method using the sliding contact as already described for an accumulator necessitates the use of a spool at one end of the bridge wire, which contains thirteen times the resistance of the bridge wire. In this way the cell is connected through 700 ohms (14×50) so that its electromotive force remains constant during the operation. By this, however, the drop in potential at the ends of the wire, with a Leclanché cell (1.4 volts), is only 0.1 volt, so that nothing larger than that can be measured, unless some elaborate device is provided by which another known electromotive force may be placed against the one to be

1 Hand- und Hilfsbuch zur Ausführung physico-chemischer Messungen, 252-253.
2 Ostwald: Grundriss der allgemeinen Chemie, 3d Ed., 433 (1899).

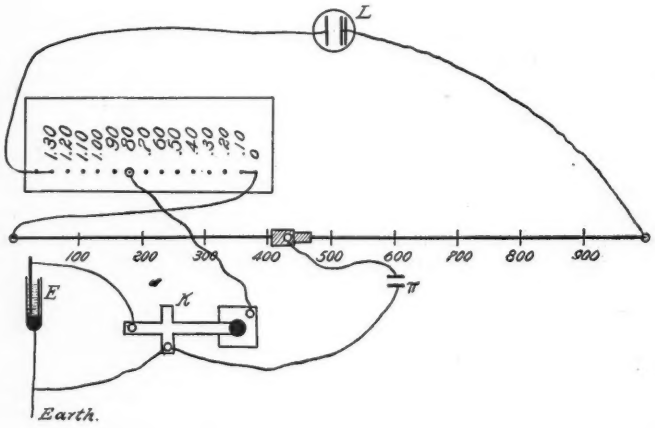
measured so as to make the difference between the two less than 0.1 volt. The accuracy of the arrangement, however, is great, for each millimeter represents 0.0001 volt if the electrometer is sufficiently delicate.

In the other method the cell is closed through a resistance box of 1000 ohms provided with nine coils of 100 ohms and ten of 10 ohms each. If the Leclanché cell is cut down to one volt by a suitable resistance, then each of the 10-ohm coils represents 0.01 volt, while each of the 100-ohm coils represents 0.1 volt. By means of two plugs, any fraction of the 1 volt may thus be placed against the electromotive force to be measured until it is compensated. Thousandths of a volt may be approximated by the movement of the meniscus of the electrometer in opposite directions, caused by the connection first to a 10-ohm coil which is just too high, and then to one which is just too low. This, however, is not to be used with very delicate electrometers for 0.01 volt may cause the meniscus to go out of the field. By the box method, then, it is possible to measure any electromotive force, even above 1 volt if a battery of 1-volt cells is at hand, with an accuracy of 0.01 volt and to approximate to 0.001 volt.

We see then that the two methods separately give satisfactory results, but that it is inconvenient, to say the least, to measure anything above 0.1 volt, with an accuracy of more than about 0.002 volt. The object of this paper is to describe a method which can take the place of both those described, and measure directly, if the electrometer is delicate enough, any electromotive force with an accuracy of 0.001 volt, and can also be used at any time for rougher work just as conveniently as the box method.

The current goes first through a box in which there are 13 coils of wire and then through a bridge wire of manganine (1 meter $\times$ 0.1 mm., resistance 50 ohms). Each of the 13 coils is of the same resistance as the wire on the bridge and may be made up of an equal length of the same wire properly insulated. On the wire there is a slider which is always in contact with the wire, while any number of the 13 coils can be brought into use in the same way as in the case of the box already mentioned. By this arrangement we have what is practically a bridge 14 meters

long of which the one meter laid out can be made any fourteenth from 1 to 14. The wire from the plug on the coils and the one from the sliding contact are treated just as those on the box are (see figure). To make a determination, the slide on the wire is placed at one end and the plug connected with the coils is moved until one post gives too great an electromotive force while the one next below it gives too small a one. The plug is then left on this latter and the sliding contact on the bridge wire



is moved until the meniscus in the electrometer is motionless when the key is pressed. To the number opposite the coil, is then added the same number of ten-thousandths as there are millimeters in the reading on the bridge. This number when multiplied by the total drop of potential at the connections to the Leclanché gives the value in volts. Possibly the use of a storage cell in the way described is to be preferred; although these cells are uncertain as a rule in their results, still this method just described has received a good trial and can be recommended whenever a primary cell is to be used.

[CONTRIBUTION FROM THE LABORATORY OF ANALYTICAL AND APPLIED CHEMISTRY, UNIVERSITY OF MICHIGAN.]

THE THERMOCHEMISTRY OF IRON AND STEEL.

[A WITHDRAWAL.]

BY E. D. CAMPBELL.

Received February 24, 1900.

IN 1897 I published in connection with Mr. F. Thompson an article entitled "A Preliminary Thermochemical Study of Iron and Steel."[1] In this article some of the results given were so unusual, that it was deemed desirable to continue the work along the same lines of investigation. The work was taken up again in the autumn of 1897 by Mr. W. E. Hartman. The first experiments undertaken were to verify the results reported in our first paper as having been obtained by Mr. Thompson. Mr. Hartman was unable to duplicate the results obtained by Mr. Thompson and as a result of this I published "A Correction," in this Journal.[2]

During the past two years my three assistants, Messrs. W. E. Hartman, Carl Sundstrom, and E. C. Champion have worked independently in an effort to explain the very unusual results reported in our first paper. Our efforts have been towards eliminating the sources of error as much as possible; to this end the calorimeter employed has been improved in many of its mechanical details, the time of solution has been reduced to usually less than four minutes. The rate of loss by radiation for each 0.1° has been determined as well as the slight gain in heat due to oxidation of cuprous chloride by dissolved air. With the most careful manipulation the difference between duplicate determinations could be kept down below 1 per cent. of the observed amount.

The first experiments undertaken were to determine the influence of the amount of free hydrochloric acid in the solution of ammonium cupric chloride employed. An interesting fact was developed at this point; it was found that if pure carbide of iron, $(CFe_3)_n$, isolated by electrolysis from annealed steel, was added to neutral ammonium copper chloride there was little or no action, the thermometer in the calorimeter rising less than 0.01° C. in five minutes; if, however, the ammonium copper chloride solution

[1] This Journal, 19, 754.

[2] *Ibid.*, 20, 78.

contained 0.09 per cent. of free hydrochloric acid, there was marked action, and with 0.46 per cent. of free hydrochloric acid, solution of 1 gram of carbide was complete in two minutes.

Other experiments were made with increasing amounts of free hydrochloric acid up to 4 per cent., the amount used in our previous work, and although it was found that some free hydrochloric acid is necessary in order to obtain complete and rapid solution, the amount of free acid up to 4 per cent. did not appreciably influence the amount of heat evolved; practically all of the iron was dissolved by its reaction with cupric chloride and not by direct solution in hydrochloric acid. The solution finally adopted for all of the later work contained 0.84 per cent. of free hydrochloric acid.

The difficult solubility of carbide of iron in neutral ammonium cupric chloride will easily account for the results obtained by Osmond quoted in our first paper. These results go to show that if steel be quenched or cold-rolled the heat of solution is thereby markedly increased. The effect of heating and quenching steel as well as of cold-rolling is to render the carbide much more easily soluble in neutral solution than when existing in annealed metal.

The results of the experiments carried on during the past two years by Messrs. Hartman, Sundstrom, and Champion have agreed with each other within the limits of experimental error. These results all go to prove that the heat of solution of steel determined in slightly acid ammonium copper chloride is not varied at the outside more than 2 per cent. by variation in the heat or mechanical treatment of the sample nor by variations in chemical composition within the limits of ordinary steel.

In view of these later experiments it must be acknowledged that the results reported in our first paper have no foundations in fact, and I would therefore request that they be considered, if possible, as withdrawn.

I regret that results of experimentation which have not been confirmed by a second worker, should have been published from this laboratory.

ANN ARBOR, MICH., February 10, 1900.

[EDITORIAL NOTE: It would be unfair to print the above without reminding the reader that Dr. Campbell's eyesight was destroyed several years since in a laboratory accident, and in consequence he has since then been entirely dependent upon others in this respect].

[CONTRIBUTION FROM THE DEPARTMENT OF FOOD AND DRUG INSPECTION OF THE MASSACHUSETTS STATE BOARD OF HEALTH.]

FOREIGN COLORING-MATTER IN MILK.

BY ALBERT E. LEACH.

Received March 15, 1900.

THE employment of artificial color by dishonest dealers to improve the appearance of milk has been practiced for many years, and while by no means as prevalent now as formerly, by reason of the stringent laws passed by various states regulating the sale of milk, the practice even to-day is by no means rare. Even in Massachusetts, which of all states is foremost in prosecuting the milk laws, artificially colored milks are occasionally found. Statistics of the Massachusetts State Board of Health show that out of 23,098 samples of milk collected throughout the state and analyzed during five years (from 1894 to 1898 inclusive), 151 samples or 0.6 per cent. were found to contain foreign coloring-matter. Of these samples, about 88 per cent. contained annatto, approximately 10 per cent. were found with an aniline orange, and about 2 per cent. with caramel.

Until comparatively recently, annatto was employed almost exclusively for this purpose. Caramel is least desirable of all the above colors from the point of view of the milk dealer, in that it is difficult to imitate with it the natural milk color by reason of the fact that the caramel color has too much of the brown and too little of the yellow in its composition. Annatto, on the other hand, when judiciously used and with the right dilution, gives a very rich, creamy appearance to the milk even when watered, which accounts for its popularity as a milk adulterant. Of late, however, the use of an orange aniline has been on the increase, and so far as a close imitation of the cream color is concerned, it is quite as efficient as annatto.

It is unfortunate for the milkman that artificial color of any kind is not analogous to the natural color of milk, which confines itself so largely to the cream. The artificial color, on the contrary, is dissipated through the whole body of the milk, so that when the cream has risen in a milk thus colored, the underlying layers, instead of showing the familiar bluish tint of skimmed milk, are still distinctly tinged below the layer of the fat, espe-

cially if any considerable quantity of the color has been used. This distinctive appearance is in itself often sufficient to direct the attention of the analyst to an artificially colored milk in the course of handling a large number of samples.

The addition of artificial color to milk is in most instances employed as a means of covering up evidences of watering, but this is not true in all cases. About 95 per cent. of the milks found colored in Massachusetts show, on analysis, the fraudulent addition of water. On the other hand, an orange aniline color was found by the writer in a milk containing over 17 per cent. of total solids, a conviction being secured on this case in court.

As to the nature of the orange aniline preparations employed for coloring milk, a few samples of these commercial "milk improvers" have fallen into the hands of the Department of Food and Drug Inspection of the Massachusetts Board of Health, and have proved, on examination, to be mixtures of two or more members of the diazo compounds of aniline. A mixture of what is known to the trade as "Orange G" and "Fast Yellow" gives a color which is practically identical with one of these preparations secured from a milk dealer and formerly used by him.

For purposes of prosecution or otherwise the generic name of "aniline orange" has been applied to this class of dyes in milk, and whatever particular mixture has been employed to make up the color, the tests which are given below have never failed to detect it when present in the milk.

The general scheme employed by the writer for the examination of milk samples suspected of being colored is as follows: About 150 cc. of the milk are curdled by the aid of heat and acetic acid, preferably in a porcelain casserole over a Bunsen flame. By the aid of a stirring rod, the curd can nearly always be gathered into one mass, which is much the easiest method of separation, the whey being simply poured off. If, however, the curd is too finely divided in the whey, the separation is effected by straining through a sieve or colander. All of the annatto or of the aniline orange present in the milk treated would be found in the curd, and part of the caramel. The curd, pressed free from adhering liquid, is picked apart, if necessary, and shaken with ether in a corked flask, in which it is allowed to soak for

several hours or until all the fat has been extracted and with it the annatto. If the milk is uncolored, or has been colored with annatto, on pouring off the ether the curd should be left perfectly white. If, on the other hand, aniline orange or caramel has been used, after pouring off the ether the curd will be colored more or less deeply depending on the amount of color employed. In other words, of the three colors annatto, caramel, and aniline orange, the annatto only is extracted by the ether. If caramel has been used, the curd will have a brown color at this stage; if aniline orange, the color of the curd will be a more or less bright orange.

The ether extract, containing the fat and the annatto, if present, is evaporated on the water-bath, the residue is made alkaline with sodium hydroxide and poured upon a small, *wet* filter, which will hold back the fat and, as the filtrate passes through, will allow the annatto, if present, to permeate the pores of the filter. On washing off the fat gently under the water tap, all the annatto of the milk used for the test will be found to have been concentrated on the filter, giving it an orange color, tolerably permanent and varying in depth with the amount of annatto present. The confirmatory test for annatto with stannous chloride may afterward be applied to the colored filter, producing the characteristic pink color.

The fat-free curd, if colored after the ether has been poured off, is examined further for caramel or aniline orange by placing a portion of the curd in a test-tube and shaking vigorously with concentrated hydrochloric acid. If the color is caramel, the acid solution of the colored curd will gradually turn a deep blue on shaking, as would also the white fat-free curd of an uncolored milk, the blue coloration being formed in a very few minutes, if the fat has been *thoroughly* extracted from the curd; indeed it seems to be absolutely essential for the prompt formation of the blue color in the acid solution that the curd be free from fat. Gentle heat will hasten the reaction. It should be noted that it is only when the blue coloration of the acid occurs in connection with a *colored* curd that caramel is to be suspected, and if much caramel be present the coloration of the acid solution will be a brownish blue. If the above treatment indicates caramel,

it would be well to confirm its presence by any of the usual tests on a fresh sample of the milk.[1]

If the milk has been colored with aniline orange, the colored curd, on applying the strong hydrochloric acid in the test-tube, will *immediately* turn pink. In the case of the caramel, the color of the curd itself remains unchanged, the solution only turning blue and that gradually; on the contrary with the aniline orange the curd itself takes the pink color the moment the acid touches it. If a large amount of the aniline orange has been used in the milk, the curd will sometimes show the pink coloration when hydrochloric acid is applied directly to it, before treatment with ether, but the color reaction with the fat-free curd is very delicate and unmistakeable.

SUMMARY OF SCHEME FOR COLOR ANALYSIS.

Curdle 150 cc. milk in casserole with heat and acetic acid. Gather curd in one mass. Pour off whey, or strain if curd is finely divided. Macerate curd with ether in corked flask. Pour off ether.

Ether Extract.	**Extracted Curd.**	
Evaporate off ether, treat residue with NaOH and pour on wetted filter. After the solution has passed through, wash off fat and dry filter, which if colored orange, indicates presence of annatto. (Confirm by $SnCl_2$).	(1) *If Colorless.* — Indicates presence of no foreign color other than in ether extract. (2) *If Orange or Brownish.*—Indicates presence of aniline orange or caramel. Shake curd in test-tube with concentrated hydrochloric acid.	
	If solution *gradually* turns blue; indicative of caramel. (Confirm by testing for caramel in whey of original milk.)	If orange curd *immediately* turns pink; indicative of aniline orange.

THE REPEATED USE OF THE DOUBLE CHLORIDE OF COPPER AND POTASSIUM FOR THE SOLUTION OF STEEL OR IRON IN ESTIMATING CARBON.[2]

BY GEO. WM. SARGENT.

Received March 20, 1900.

IN the *Chemical News*, Vol. 79, p. 169, which appeared April 14 of last year, there is an article headed: "The Estimation of

[1] See Nineteenth Annual Report of the Mass. State Board of Health (1887), p. 183.

[2] Read at the March meeting of the Philadelphia Section of the American Chemical Society.

Carbon in Steel; Apparatus and Materials," signed J. T., in the course of which, it is stated, that the copper ammonium chloride may be reused as many as eight times, provided it is oxidized by drawing air through it after each solution, and provided the practice of allowing the sample to dissolve over night, is adopted. After the operation had been repeated four or five times, there was a decided decrease in the rate of solution and the speed of filtering, therefore it was practicable to use it successively but three or four times, unless the solution of the drillings was made in neutral copper ammonium chloride by shaking in a stoppered flask, when upon removing the carbon and oxidizing, the clear green liquid could be filtered from the iron oxide and reused *ad infinitem*.

Copper potassium chloride, owing to its freedom from organic matter, has supplanted the ammonium salt. Most chemists use the former in a hydrochloric acid solution,[1] when by the aid of a stirring machine, the drillings are dissolved in less than an hour. The reaction is expressed in the following equation:

$$Fe + CuCl_2 = FeCl_2 + Cu \text{ and } Cu + CuCl_2 = Cu_2Cl_2.$$

If now the cuprous chloride be oxidized to cupric, there is no reason why the double chloride solution should not be used repeatedly until the accumulated iron salts become too great. As stated above, this has been done, but the time consumed in oxidizing by a current of air was too long,—several days of an almost continuous current of air through a liter of the acid double chloride failed to completely oxidize the copper salt. The source of my air current was a filter pump, making the waste of water very considerable.

The oxidation was then attempted by the electric current using a cell such as is used for electrolytic oxidations. The result was fairly satisfactory, 3 quarts being oxidized in two days' time; but both these methods yield the cupric chloride at the expense of the hydrochloric acid:

$$O + 2HCl + Cu_2Cl_2 = H_2O + 2CuCl_2 \text{ and } 2HCl + Cu_2Cl_2 = H_2$$

at the cathode and cupric chloride at the anode. Not knowing the quantity of acid consumed in the oxidation, without keeping careful account of the drillings and solution used, it would be

[1] See "The Chemical Analysis of Iron," by Blair.

difficult to tell just how much acid should be added after each oxidation in order to have the double chloride of the proper strength for the next solution. Again the chlorine formed at the anode would attack it. Therefore, I decided to try the effect of chlorinating the solution direct.

The result has been most agreeable. At the present time we have three bottles of 3 quarts' capacity; in the one, the filtered double chloride ready for the solution of the drillings is kept; the second receives the undiluted filtrate from the carbon, while the third, filled with the filtrates, stands in the corner of the hood with a current of chlorine gas passing through it. It requires just a day to chlorinate 3 quarts, and that is about the amount consumed each day. When chlorinated the solution, instead of being of a dirty brown, has almost the original color of copper potassium chloride. After standing over night in the hood and being filtered, the objectionable odor of chlorine is gone and the solution is again ready for use. The chlorinated double chloride is more energetic in its solvent action. In some instances the solution of the drillings has been accomplished in fifteen minutes.

As many as eleven solutions have been made with one quantity of the double chloride, and the time required for the eleventh solution and filtration was very little longer than for the first.

The following results were obtained by the successive use of the same solution:

Number of sample.	Carbon. Per cent.	Number of times the double chloride solution had been previously used.
17	0.864	None
"	0.864	1
1922	0.605	None
"	0.614	2
1930	0.755	None
"	0.752	3
1942	0.410	None
"	0.411	4
1944CX	1.608	None
"	1.614	6
1991	0.385	None
"	0.384	7
1969	0.613	None
"	0.615	11

The saving effected by reusing the copper potassium chloride solution is no inconsiderable amount, especially where much of the salt is used. Roughly estimating, 1 pound of black oxide of manganese, and 1.5 pounds of hydrochloric acid, are sufficient to reconvert 3 quarts of the double chloride, worth about $1.00.

LABORATORY OF THE CARPENTER STEEL CO.,
READING, PA., March, 1900.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CASE SCHOOL OF APPLIED SCIENCE, NO. 33.]

ON THE DETERMINATION OF CARBON AND HYDROGEN BY COMBUSTION IN OXYGEN USING COPPER OXIDE.[1]

BY CHARLES F. MABERY AND WILLIAM R. CLYMER.

Received March 15, 1900.

IN a former paper[2] on combustion with copper oxide it was stated that some experiments were in progress to determine the conditions of efficiency, and limits of accuracy when applied to the analysis of oils containing only carbon and hydrogen.

In the long and tedious experience in the analysis of the great number of hydrocarbons that have been under examination in this laboratory, there have been ample opportunities to observe the working details in the hands of a large number of operators who have served at different times as assistants.

The difficulties in the way of securing results with oils containing only carbon and hydrogen, that will calculate closely to 100 per cent., are much greater than with substances containing smaller proportions of these elements, and require great skill and patience on the part of the operator.

Our experience shows that copper oxide is reliable after it has been brought to a constant condition by blank trials. The gases that are evolved in the combustion of some of the hydrocarbons require the highest temperature in presence of oxygen that can be brought to bear, without too great strain on the combustion tube.

The first essential is a drying apparatus that will remove water and carbon dioxide from air and oxygen, and remain in good condition without too frequent renewal. The apparatus now in

[1] The work described in this paper formed the subject of a thesis by Mr. Clymer for the Degree of Bachelor of Science.

[2] This Journal, 20, 510.

use in this laboratory which does not need renewal oftener than once in a year or two, consists of two pieces of combustion tubing 1.75 meters long, with a bend 30 cm. from one end, with an angle of about 105°, and placed on the wall in front of the combustion furnaces. One of these tubes for air and another for oxygen are nearly filled with broken glass and concentrated sulphuric acid. A second set of tubes are filled to the same extent with glass and a 40 per cent. solution of potassium hydroxide, one for air and another for oxygen. Air is supplied from a large iron tank under water pressure and the flow is regulated by a mercury seal. Oxygen is supplied from a smaller tank under water pressure regulated by an overflow.

For absorbing water from combustion, there is no more convenient nor efficient means than concentrated sulphuric acid. One point must be borne in mind and that is the retention of carbon dioxide by the acid. Since it is well known that concentrated sulphuric acid dissolves carbon dioxide to the extent of 75 per cent. of its volume, some experiments were made to ascertain just the conditions necessary to avoid retention in analysis.

In one experiment dry carbon dioxide was passed for one hour through 2 cc. of the acid in a U-tube, just sealed by the acid. Then dry air was passed through the acid for two hours, when the tube was found to have gained 1 milligram in weight. At the end of another hour the gain was reduced to 0.0008 gram, and at the end of the third hour the weight was just the same as at the beginning of the experiment.

In a second experiment conducted in the same manner the original weight was reached in two and one-half hours. In a third experiment a larger sulphuric acid tube was used containing 7 cc. of the concentrated acid. After passing carbon dioxide for one-half hour and air for one hour and fifteen minutes the gain in weight was 0.0075. In continuing the passage of air at the rate of 500 cc. per hour for different lengths of time the following results were obtained.

Minutes.	Increase.
15	0.0058
15	0.0047
15	0.0037
1 hour	0.0029
1 "	0.0018
1 "	0.0018
1 "	0.0001

It was, therefore, only after air had been passed five hours that the weight was reduced to the original. In a third experiment a potash bulb was placed in front of the sulphuric acid tube, and carbon dioxide was passed one hour, and air for one hour. The potash bulb was now attached and the gain in weight (with air) compared with the loss in the acid tube.

Hour.	Loss in acid tube.	Gain in potash tube.
I	0.0014	0.0014
I	0.0008	0.0007
I	0.0005	0.0005
I	0.0002	0.0002
I	0.0000	0.0001

In a fourth experiment, carbon dioxide was passed for one hour through 2 cc. of acid, then air for one hour, then air for one hour more and weighed; the gain in weight was 0.0007 gram. Carbon dioxide was then passed for one hour and air for another hour, then at the end of a second hour the weight was 0.0004 gram. In three repetitions the gains were respectively 0.0006, 0.0004, and 0.0006 gram showing that passing air the same length of time leaves the same weight of carbon dioxide in the acid. These experiments indicate that when a small volume of acid, 2 to 3 cc., is used with the large volume of oxygen and air used to expel carbon dioxide from the tube, very little of the gas remains dissolved in the acid. But with larger volumes of the acid there is danger of retention of carbon dioxide.

In testing the capacity of sulphuric acid to retain moisture, moist air was passed through 2 to 3 cc. of the acid at the rate of 1100 cc. per hour for four hours. At this rate the bubbles cannot be counted. In front of the sulphuric acid tube was placed a high tube filled with phosphorus pentoxide but there was no gain in the latter tube. There is therefore no danger of loss in water if sulphuric acid is used. The only value of this experiment was to ascertain the conditions since Morley showed several years ago that sulphuric acid is a most efficient drying agent. The form of sulphuric acid tube we have used for several years has a bulb for collecting the greater part of the condensed water which is poured out after weighing. The forward bend of the U is 10 cm. in height from the bottom and a side tube is attached for connection to the potash bulb. When containing 3 cc. of concentrated acid, and 0.2000 gram water is weighed in each

combustion, the tube may be safely used without replacing the acid in ten or twelve combustions and probably longer. That sulphuric acid is preferable to calcium chloride has frequently been shown, since the best fused calcium chloride may contain basic chloride which retains carbon dioxide. It was shown by Winkler[1] that lime in the chloride cannot be completely saturated by carbon dioxide, since the inside of the granules remain caustic for a long time.

It is doubtful whether there is a more convenient apparatus than the Geissler potash bulb for the absorption of carbon dioxide, especially if the substance analyzed consists, for the most part, of carbon and hydrogen. There is no danger of loss of carbon dioxide if the solution of $33\frac{1}{3}$ per cent. potash be not used in more than four or five analyses. But there is danger of loss of moisture from the potash bulb unless care is taken to prevent it.

Some experiments were made to ascertain the conditions of safety. In one experiment the calcium chloride tube in front of the potash bulb was filled with freshly fused calcium chloride, broken to the size of grains of rice. Air was passed through at the rate of 550 cc. per hour with no loss in weight of the potash bulb, and the result was verified by placing a sulphuric acid tube in front of the calcium chloride tube which showed no gain in weight. Any faster rate than this showed a loss in the potash bulb and a corresponding gain in the sulphuric acid tube. On replacing the granular calcium chloride with other more finely ground, in a slightly longer tube, and passing air at the rate of 1050 cc. an hour, or 120 bubbles a minute, there was no change in weights. With a calcium tube of common length, 6 cm., a rate of 880 cc. per hour caused a loss of 0.0004 gram in the potash bulb and a gain of 0.0005 gram in the sulphuric acid tube. It is therefore safe to pass 500 cc. per minute through a tube filled with freshly fused finely granular calcium chloride. Such calcium chloride may be used in a considerable number of analyses. This rate can not be exceeded in the combustion of oils that are in part or all volatile without decomposition, or that yield gaseous products in burning. But this rate is in any sense in excess of the rate of evolution of gas from the combustion, since the carbon dioxide is, for the most part, immediately absorbed as

[1] *Ztschr. anal. Chem.*, 545, 1882.

soon as it meets the potash solution. By replacing the fused calcium chloride with phosphorus pentoxide, there was no loss even when the rate exceeded 1000 cc. per hour, or 120 bubbles a second. But the oxide offers no advantages over the fused chloride in ordinary analysis.

In preparing for a long series of combustions a combustion tube should be selected that promises to stand 50 to 100 analyses, since it requires a long time to get the tube and its contents and connections in good working order. A long time is required to remove all the volatile impurities from the best copper oxide, and the moisture from the tube and oxide. Rubber stoppers are the only means for satisfactory connections, but before they become constant in weight probably some of the sulphur must be volatilized and moisture expelled. It is therefore necessary to test carefully all parts of the apparatus by means of blank experiments in the beginning, and even after the apparatus becomes constant it is well occasionally to apply a blank test.

In conducting analyses of such bodies as the high-boiling constituents of petroleum, the closest attention to details is necessary. The tube must be as hot as it will stand, and yet not hot enough to lessen its durability, on account of the labor involved in getting it in good condition. If the combustion tube be filled with oxygen before the substance is inserted and the rate of volatilization be carefully controlled, any hydrocarbon may be burned in a furnace with 20 burners. Many analyses were lost before these conditions were fully understood. In view of the possibility that a longer combustion tube might insure complete combustion and shorten the time of the analysis, two furnaces were placed together, and a tube nearly two meters in length was used. But the results were not more satisfactory than with a tube of ordinary length.

As a general summary of what is necessary to insure desirable accuracy in such determinations, it must be fully understood at the outset that no operation in analytical chemistry demands greater precautions, closer attention to details, or more skill and patience on the part of the operator to insure results within 0.20 per cent. of the maximum 100 per cent. in substances composed solely of carbon and hydrogen, such as petroleum oils.

In view of the great amount of work that will have to be done in determining the constitution of the large number of hydrocarbons with high molecular weights in Pennsylvania, California, and other petroleums, it would be a great advantage if a method for the determination of carbon and hydrogen could be devised that would avoid the tedious routine of the present method. But with present knowledge of this subject this method is probably all that can be hoped for. The Geissler potash bulb and the sulphuric acid tube seem to be as convenient forms as can be devised and they are capable, as shown above, of retaining carbon dioxide and water with as rapid delivery as is consistent with complete combustion. Rubber corks are objectionable, but they are the only convenient and reliable means of connection available.

We have tried successfully weighing the bulbs full of oxygen, thus avoiding the expulsion of oxygen by air. But since the time necessary to carry forward all the carbon dioxide is equivalent to that necessary to displace oxygen by air, there is nothing gained by weighing the bulbs filled with oxygen. The precautions necessary to insure cleanliness of the bulbs and constant conditions of moisture and temperature in weighing must be carefully observed.

CIDER VINEGAR: ITS SOLIDS AND ASH.

By R. E. Doolittle and W. H. Hess.

Received March 15, 1900.

DURING the past few years the question of vinegar adulteration has received considerable attention from food chemists. Heretofore the sophistication has consisted almost entirely of the sale of colored distilled vinegar for pure fermented apple juice. As distilled vinegar contains little or no solids or ash this fraud was easily detected by very simple determinations. During the year 1899, however, there appeared for sale on the markets of this state, vinegar containing the necessary amount of solids and ash required by the statute for cider vinegar; but on ordinary analysis of this the solids and ash did not have the usual appearance of solids and ash of vinegar from pure apple juice. It was to ascertain the character of these vinegars

that the investigation of the solids and ash of cider vinegar was made.

THE SOLIDS.

The solids of pure cider vinegar consist of glycerol, albuminous substances, gums, malic and other organic acids, and mineral matter. The solids of pure cider vinegar give no rotation with the polariscope and little or no reducing action on Fehling solution after the customary clarification with lead acetate. Pure cider vinegar gives with lead acetate a heavy, flaky, light reddish brown-colored precipitate, which carries down with it all the coloring-matter leaving the solution above clear and nearly colorless. For analysis of solids 1000 cc. of pure cider vinegar was evaporated to a thick sirup on a water-bath and this residue taken up several times with distilled water and the water evaporated off to remove acetic acid. The suspected vinegars were treated in the same manner. The appearance of the solids on evaporation should be noted. Pure cider vinegar solids have a pleasant baked apple odor and are light and foamy in appearance. The spurious vinegars gave solids like molasses in appearance and of sharp acid odor. These residues gave the following results on analysis :

	Pure cider vinegar solids.	Apple pomace vinegar solids.	Suspected vinegar. (1)	Suspected vinegar. (2)	Boiled cider.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Reducing sugar before inversion	0 to 14	0	42.88	56.82	61.12
" " after "	0 to 10	0	33.36	57.04	66.45
Polarization before inversion	0	0	+40.7°	−31.14°	−17.9°
" after "	0	0	+38.8°	−34.25°	−25.0°

THE ASH, OR MINERAL MATTER.

The ash, or mineral matter, of pure cider vinegar consists principally of potash with small amounts of sulphuric anhydride, phosphoric acid, alumina, lime, magnesia, etc. The total amount should not be less than 0.25 per cent. For analysis, 100 cc. of the vinegar are taken for the determination of the total solids and ash in the usual way. The ash is dissolved in dilute hydrochloric acid and quantitative analysis made by the usual

method. The results in the following table are given as the average composition as determined by a large number of analyses. The suspected vinegars, Nos. "1" and "2," and also the ash of vinegar made by repressing moist fermented apple pomace, are given for comparison.

	Pure cider vinegar ash. Per cent.	Apple pomace vinegar ash. Per cent.	Vinegar. (1) Per cent.	Vinegar. (2) Per cent.
Calcium Oxide (CaO)	3.40 to 8.21	4.73	4.70	37.95
Magnesium oxide (MgO) ...	1.88 to 3.44	4.12	2.00	2.22
Potassium oxide (K_2O)	46.33 to 65.64	37.00	None	7.84
Sodium oxide (Na_2O).....	Trace to trace	Trace	49.71	Trace
Sulphuric anhydride (SO_3) .	4.66 to 16.29	34.78	27.04	12.74
Phosphoric anhydride (P_2O_5.	3.29 to 6.66	9.66	0.005	1.82
Iron oxide (Fe_2O_3)	None to trace	Trace	Trace	1.60
Carbon dioxide, loss, etc....	40.44 to 0	9.61	16.54	35.83

The results of these analyses plainly showed that suspected vinegar No. 1 was composed of dilute acetic acid, glucose, and soda-ash. Suspected vinegar No. 2 was a mixture of acetic acid, boiled cider, and lime.

LABORATORY MICHIGAN DAIRY AND FOOD DEPARTMENT,
March 12, 1900.

NOTES.

Test for Tin.—I have found the blue color produced by the action of stannous chloride upon ammonium molybdate to serve as a very delicate test for tin; and have had my students use it for the last few months with very good results. In working this process one should go through the usual separation, filter off the black flakes, dissolve them in hydrochloric acid, then take a few drops of this solution and add a little water and then some ammonium molybdate. Blue color shows the presence of tin.

To determine the delicacy of the test, I used a standard solution of stannous chloride, and noticed results obtained from the mercuric chloride and ammonium molybdate tests.

Strong solution of $SnCl_2$ gives a heavy blue precipitate; with mercuric chloride a heavy white precipitate.

A solution of $SnCl_2$ containing 0.000021 gram to 1 cc. gives a deep blue color; with mercuric chloride a faint cloudiness.

A solution of $SnCl_2$ containing 0.0000042 gram to 1 cc. gives a

faint blue color with ammonium molybdate; with mercuric chloride not even a trace of cloudiness.

I find that the ammonium molybdate as prepared in the laboratory gives the best results.

ALLEN ROGERS.

Professor C. F. Mabery has sent to the Paris Exposition, at the invitation of the United States Geological Survey, 150 specimens of products from petroleum, illustrating the composition of Pennsylvania, Ohio, Canadian, California, South American, and Japanese petroleums, and specimens of nitrogen compounds from California petroleum, and sulphur compounds from Canadian petroleum. Other specimens illustrate the composition of paraffin.

NEW BOOKS.

DESCRIPTIVE GENERAL CHEMISTRY. BY S. E. TILLMAN, Professor of Chemistry, Mineralogy and Geology, United States Military Academy. Second Edition. New York: John Wiley and Sons. London: Chapman and Hall. x + 429 pp. 8vo. cloth. Price, $3.00.

This book was written to meet the requirements for a text-book on chemistry at the Military Academy at West Point. It aims to give in compact form the salient facts of chemistry that the professional soldier ought to know. The time available for the study of chemistry at the Academy is a little less than two-hundred hours, so that in order to cover the subject but a very limited amount of laboratory work can be undertaken. The chief aim therefore is to impart to the student the necessary information, rather than to make the element of mental discipline the more prominent one. Study of a text-book accompanied by recitations and experimental and explanatory lectures together with a small amount of selected laboratory work consequently make up the course pursued.

The book is divided into six chapters which are as follows: I. Essential Principles of Chemistry, pp. 1–58; II. Affinity, pp. 59–81; III. Non-metals, pp. 82–192; IV. Metals, pp. 193–310; V. Organic chemistry, pp. 311–356; VI. Applications of Chemistry, pp. 357–411. In the first chapter the general principles of chemistry are stated, while in Chapter II, the law of mass action, strength of acids and bases, theory of solution, electrolysis,

thermal chemistry, periodic law, etc., are discussed. All this is of course done very briefly, and in connection with these two chapters, in particular, the explanatory lectures mentioned above will no doubt be very essential. Chapters III and IV are not unlike chapters on the same subjects found in other texts. In the 45 pages devoted to organic chemistry only a number of groups of such compounds as are of the utmost practical importance to the particular student for whom the text is intended could be considered. The applications of chemistry in the last chapter include calorific value, explosives, fixed oils, dyeing, and the manufacture of glass, pottery, coal-gas, beer, distilled liquors, wine, bread, soap, leather, and cheese. While this chapter is devoted to practical applications exclusively, the author has not neglected to seize the opportunities of pointing out numerous practical applications in the chapters preceding.

The author has earnestly endeavored to incorporate recent discoveries and theories into his book. While his statements are generally clear, they are unfortunately not always free from inaccuracies. Only a few instances of this will here be mentioned. So on p. 69 the author neglects to point out that the assumption of electrical charges on the ions is a salient part of the theory of electrolytic dissociation, but simply adds in a footnote that the ions are probably electrically charged. On p. 71 heat of formation is confused with the thermal change that accompanies a chemical reaction. On p. 99 the statement is made that the form of the crystal is due to water of crystallization.

The book as a whole is good for the purpose for which it was written. The selection of the topics treated (upon which so much depends in a case like this) is wise; and the presentation is good considering the very condensed form necessitated. There can be no doubt that the book will meet the special needs of the students at the Military Academy better than any other textbook that is available at present.

LOUIS KAHLENBERG.

LEITFADEN FÜR DEN UNTERRICHT IN DER ANORGANISCHEN CHEMIE. BY DR. JOACHIM SPERBER. Zürich: Verlag von E. Speidel. 1899. 119 pp.

This is the first part of an extended treatise on inorganic chemistry. It treats of the usual gaseous elements, the halogens, and the non-metals. The author has applied the

inductive method to the teaching of inorganic chemistry. From simple and well chosen experiments, the fundamental principles are derived. Each set of experiments is chosen with the idea of illustrating some particular law, and is given in advance of the statement of the law itself. The laws of definite and multiple proportions, and Avogadro's law, are all established by experiment before the detailed study of the elements is begun. The order in which the separate elements are taken up is unusual. Beginning with hydrogen, the elements fluorine, chlorine, bromine, and iodine are studied, and then their hydrogen compounds. Subsequently oxygen, sulphur, selenium, and tellurium are taken up, and followed by their hydrogen compounds. Then comes the group of trivalent elements, nitrogen, phosphorus, arsenic, followed by the tetravalent carbon and silicon.

The statements in regard to the occurrence, preparation, properties, and uses of the separate elements are concise, accurate, and comprehensive. Separate theoretical considerations such as the dissociation of substances by heat, the determination of molecular weights, etc., are discussed in appropriate places, which tend to emphasize them and to show their applicability. The book contains the most recent discoveries. The illustrations are frequent, and exceptionally good. HENRY FAY.

LEXIKON DER KOHLENSTOFF VERBINDUNGEN. VON M. M. Richter. Zweite Auflage der "Tabellen der Kohlenstoff-Verbindungen nach deren empirischer Zuzammensetzung geordnet." Hamburg und Leipzig: Leopold Voss; New York: G. E. Stechert. pp. about 3100. Price, 39 Lieferungen at M. 1.80 each.

It is, apparently, impossible to secure the adoption of a uniform system of nomenclature for carbon compounds. Indeed some chemists claim, and with good reason, that complete uniformity is not desirable. It becomes, therefore, every year more difficult to be sure of finding, in chemical literature, what is known about particular compounds. The work before us furnishes a lexicon of the carbon compounds arranged in accordance with their empirical formulas. The order is, first, that of the number of carbon atoms, second, that of the number of elements, third that of the elements other than carbon in the order:

H O N Cl Br I F S P Al.....Zr.

The only exception to a rigid use of the above classification

is in the case of salts, which are given under the corresponding acids or bases. After each empirical formula is given the percentage composition for all compounds containing only carbon, hydrogen, oxygen, and nitrogen. Then follows a list of all known isomers of the given composition, giving melting-points and boiling-points, references to the literature, and finally the volume and page of the last edition of "Beilstein" where the compound is described. The number of compounds included in the work is about 75,000, while the last edition of "Beilstein" includes only 57,000.

The usefulness of the principle used for registering organic compounds is so apparent that it has been adopted for the indexes of the *Berichte* and of Liebig's *Annalen*.

The literature is fully covered to the end of 1898, and yearly supplements are promised.

A few errors have been detected, but mostly where confusion exists in the literature and a critical knowledge of the relations involved was necessary to avoid mistake. Even such errors are probably rare and will seldom cause trouble in using the work.

The author complains that the failure to give empirical formulas, on the part of many writers, has added greatly to his labors and requests that such formulas be always given. In the opinion of the writer it would be a misfortune if this request should lead to the use of fewer structural formulas. The needs and advantage of the average reader are of greater importance than the time of the lexicographer. WILLIAM A. NOYES.

THE URINE AND THE CLINICAL CHEMISTRY OF THE GASTRIC CONTENTS, THE COMMON POISONS, AND MILK. By J. W. HOLLAND, M.D., Professor of Medical Chemistry and Toxicology, Jefferson Medical College of Philadelphia. Sixth edition, revised and enlarged. Philadelphia: P. Blakiston's Son & Co. 49 illustrations. Cloth. Price, $1.00 net.

This syllabus for the laboratory aims to guide the student in the chemical examinations that are of service to the physician. The methods are much the same as may be found in similar works, and, while in many instances they are well selected, they include certain methods that might better be omitted or replaced by procedures which yield results of clinical value. The brief text omits much information that would add materially to the work. It is particularly desirable to indicate more definitely to what use the results obtained by the various methods are to be

put in practice, even at the risk of adding slightly to the bulk of the text. Unfortunately misstatements are not infrequent and there is an unusual number of errors in the references.

E. E. SMITH.

ANNUAIRE DU BUREAU DES LONGITUDES, pour l'An 1900. Paris: Gauthier-Villars. 18mo. 800 pp. Price, 1.85 francs.

This handy little annual is, as its name would indicate, mostly concerned with astronomic data. The first three hundred pages are devoted to calendars, astronomic phenomena of 1900, data of all kinds concerning the sun, moon, earth, planets, stars, and comets. Then follow tables of various weights and measures, moneys, statistics of population, territory and mortality in different countries. These are followed by diverse tables, such as magnetic intensity in various parts of France; specific gravities of solids, liquids and gases; acoustic, optic, and electric data.

The scientific addenda contain a well-written article of thirty pages on "electric units," by A. Cornu; an essay of over eighty pages on "dynamo-electric machines" also by Cornu, concise but satisfactorily written, and a short essay on "the new gases of the atmosphere," by Lippmann.

Many of the tables concerning physical and chemical facts are incomplete, and do not give the very best, latest determinations. In general, the French determination only is given, whenever a datum has been determined by a Frenchman, and his value stands until some other Frenchman does it better. This may be very patriotic, but it is not scientific, or good sense.

Visitors to Paris this year will be interested in the statement that "The legal time in France is that of the observatory of Paris, and is that recorded by the dials *outside* the stations, the dials *inside* the stations being several minutes later, for purely administrative reasons!"

J. W. RICHARDS.

OPTICAL ACTIVITY AND CHEMICAL COMPOSITION. BY DR. H. LANDOLT, Professor of Chemistry in the University of Berlin. Translated with the author's permission by JOHN MCCRAE, Ph.D. London: Whittaker and Co.; New York: The Macmillan Company. 158 pp. Price, $1.00.

This little book is a translation of the eighth chapter of the well-known Graham-Otto "Lehrbuch der Chemie," which has passed through several editions. This eighth chapter was contributed by Professor Landolt who is the great authority on

everything connected with the subject of the optical activity of organic compounds. The discussion in this book covers briefly the subject of optical activity in general and the relation of this activity to the composition and structure of various groups of organic compounds. It does not deal with the practical applications of polariscopic methods at all, this larger field being fully covered by the important work of the author, "Das optische Drehungsvermoegen organischer Substanzen, und dessen praktische Anwendungen," an English translation of which is now being made by the writer of this notice.

Dr. McCrae's translation is an extremely clear and creditable one and the book will undoubtedly be found useful.

J. H. LONG.

CHEMISCH-TECHNISCHE UNTERSUCHUNGSMETHODEN. HERAUSGEGEBEN VON DR. GEORG LUNGE. Zweiter Band. 143 Abbildungen. Vierte Auflage. Berlin: Julius Springer, 1900. xii + 804 pp. Price, 16 marks.

This volume treats of Iron, by Th. Beckert; Other Metals, Metallic Salts, Dr. Pufahl; Fertilizers, Dr. O. Böttcher; Fodders, Dr. F. Barnstein; Explosives, O. Guttmann; Matches, Wladmir Jettel; Gas Manufacture, Ammonium Compounds, Dr. O. Pfeiffer; Coal Tar, Dr. H. Köhler; Inorganic Colors, Dr. Gnehm. In such a wide range of subjects some unevenness in treatment is inevitable. A careful examination of the book shows that in the main, the work has been well done though there are some omissions that will surprise the reader familiar with recent practice. For example, nothing is said of the methods for the determination of phosphorus in steel depending upon the reduction of molybdenum in the yellow precipitate and its determination by permanganate. Cupric ammonium chloride only is mentioned as a solvent for iron in carbon determinations. No reference is made either to the recent improvement in Jones' reductor or to Dr. Shimer's beautiful combustion method now so widely used. There are other omissions equally serious.

Rapid methods are absolutely essential in steel laboratories where the bulk of such work is done and any treatment which, like this, fails to give them proper prominence cannot be pronounced altogether satisfactory.

In a German book it is unusual to find so many references to American improvements. The Gooch crucible, Hoskins' gaso-

line furnace, Ricketts' rubbing plate, and Jones' reductor are all mentioned and some of them figured and there are numerous references to this Journal, to the *Journal of Analytical and Applied Chemistry*, and to the *Engineering and Mining Journal*. Drown's method for silicon is described as "Verfahren von Brown."

One feature of the book deserving of notice is the reprinting of the most useful tables on separate sheets. These are placed at the end of the book to be torn out and pasted up in the laboratory if desired. The mechanical execution of the book is excellent. The third volume is promised for the middle of 1900.

E. H.

THE GRAMMAR OF SCIENCE. By KARL PIERSON. Second edition revised and enlarged with 33 figures. London: Adam and Charles Black. 1900. New York: The Macmillan Co. 8 vo. xviii + 548 pp.

This is a metaphysical book written by a believer in scientific methods. It is divided into twelve chapters and an appendix. The chapters are entitled as follows: Introductory; The Facts of Science; The Scientific Law; Cause and Effect—Probability; Space and Time; The Geometry of Motion; Matter; The Laws of Motion; Life; Evolution (Variation and Selection); Evolution (Reproduction and Inheritance); The Classification of the Sciences; The mechanical execution of the book (printed by R. and R. Clark, Edinburgh) is superb. E. H.

ELEMENTARY CHEMISTRY FOR HIGH SCHOOLS AND ACADEMIES. By ALBERT L. AREY. C. E. Rochester High School. New York: The Macmillan Company. 1899. xi + 271 pp. Price, 90 cents.

There seems to be an increasing tendency to introduce chemistry into the secondary schools as a disciplinary study. This volume is offered as a text-book in elementary chemistry, and is an attempt to present the subject in such a manner as to develop the student's faculties for observation and interpretation. This is accomplished by making the book a laboratory guide as well as a text-book. Numerous questions on the text and the laboratory experiments are found throughout the book. They have been intelligently selected, and are of such a nature that they can be answered only by direct experiment or by analogy. Many statements of facts have purposely been omitted so that the student may be more impressed with the experiment. The experiments are well selected and well arranged.

The main portion of the book treats of the elementary laws, the preparation, properties, and reactions of the gases, non-metals and metals. No mention of the periodic law is made, and there is no attempt to show the striking analogies in the properties of the elements and their compounds. It is much to be regretted also that there is little mention of historical names. They are so intimately connected with the science that it seems a great pity to have dropped them almost entirely. The author has introduced the term *crith* as the weight of a liter of hydrogen. It does not aid in the understanding and must surely lead to confusion.

The last chapter of twenty-five pages treats briefly of qualitative analysis. In the reviewer's opinion this portion of the book should have been devoted to the study of the preparation of typical inorganic compounds. The prime object of many books of this class is to prepare the student to make *separations*. While this cannot be said of this volume, there will, nevertheless, be a strong tendency on the part of the student to anticipate qualitative analysis on account of its presence in the book.

With the exception of the criticisms made, the book is to be commended. HENRY FAY.

THE THEORY OF ELECTROLYTIC DISSOCIATION AND SOME OF ITS APPLICATIONS. By HARRY C. JONES, Associate in Physical Chemistry in Johns Hopkins University. New York: The Macmillan Company. 1900. Cloth. xii + 289 pp. Price, $1.60.

This book contains a survey of the earlier physical chemistry, an account of the origin of the theory of electrolytic dissociation together with a presentation of the evidence supporting the same, and some of the important applications of the theory.

Every student of chemistry, physics, and biology, who is not already well acquainted with the theory of electrolytic dissociation will find this an interesting and valuable book to read. The development of modern physical chemistry is, in a large measure, intimately connected with this theory. The facts that the latter has been able to explain and to correlate are many; and above all, the importance of the stimulus it has given to research can hardly be overestimated.

In this book the theory of electrolytic dissociation is viewed in its most favorable light. It must be admitted, however, that during the last year or two, facts have begun to accumulate which

the theory cannot explain. Though these facts have developed mainly from a study of non-aqueous solutions, yet in many instances the theory finds much difficulty in explaining the facts in case of aqueous solutions, especially when quantitative data are involved. It seems at present that even before the theory of electrolytic dissociation will have found its way into regular chemical text-books, it will have undergone radical modifications from its present form, or will perhaps have been superseded by more adequate explanations. LOUIS KAHLENBERG.

VICTOR V. RICHTER'S ORGANIC CHEMISTRY OR CHEMISTRY OF THE CARBON COMPOUNDS. Edited by PROF. R. ANSCHÜTZ. Authorized translation by EDGAR F. SMITH, Professor of Chemistry, University of Pennsylvania. Third American from the eighth German edition. Vol. II. Carbocyclic and Heterocyclic Series. Philadelphia: P. Blakiston's Son & Co. 1900. 671 pp. Price, $3.00.

The first volume of this work was reviewed last year.[1] About the only adverse criticism which could be made of the completed work is that the theoretical discussions are often so concise that it is almost impossible for beginners to comprehend them. It is, however, necessary, in a book of this character, to choose between a very concise style and the omission of a great deal of material which it is desirable to include. The book is, undoubtedly, much more valuable because the former alternative was chosen. The comprehensive character of the work, considering its size, is remarkable.

In discussing Ladenburg's prism formula for benzene on page 41 the author has, apparently, overlooked the fact that, since the reduction of ortho compounds gives derivatives of cyclohexane in which the substituents are combined with adjacent carbon atoms, the prism formula must be considered as positively disproved.

Professor Anschütz has availed himself of the aid of other workers who are specially conversant with particular fields and has so secured an accuracy of presentation which a single author could not hope to attain. W. A. NOYES.

AN INTRODUCTION TO PHYSICAL CHEMISTRY. By JAMES WALKER, Professor of Chemistry in University College, Dundee. New York: The Macmillan Company. 1899. 8vo. Cloth. x+335 pp. Price, $2.50.

A number of elementary treatises on physical chemistry have

[1] This Journal 21, 708.

recently appeared. Although Professor Walker's book is rather more voluminous than other works on the same subject intended for beginners, it does not pretend to give a complete or even systematic survey of physical chemistry. Its main object as expressed by the author is to be explanatory and to place the student in a position to profit by the study of the larger systematic works of Ostwald, Nernst, and van't Hoff.

The book is divided into 27 chapters; and, though the enumeration is somewhat long, there is perhaps no better way to convey an idea of the contents of this treatise than to indicate the subjects of these chapters together with the number of pages devoted to each. The chapters are as follows:—Units and Standards of Measurement, pp. 1–7; The Atomic Theory and Atomic Weights, pp. 8–21; Chemical Equations, pp. 22–26; The Simple Gas Laws, pp. 27–29; Specific Heats, pp. 30–37; The Periodic Law, pp. 38–49; Solubility, pp. 50–59; Fusion and Solidification, pp. 60–72; Vaporization and Condensation, pp. 73–83; The Kinetic Theory and Van der Waals' Equation, pp. 84–96; The Phase Rule, pp. 97–116; Thermochemical Change, pp. 117–126; Variation of Physical Properties in Homologous Series, pp. 127–135; Relation of Physical Properties to Composition and Constitution, pp. 136–147; The Properties of Dissolved Substances, pp. 148–157; Osmotic Pressure and the Gas Laws for Dilute Solutions, pp. 158–168; Deductions from the Gas Laws for Dilute Solutions, pp. 169–175; Methods of Molecular Weight Determinations, pp. 176–192; Molecular Complexity, pp. 193–200; Electrolytes and Electrolysis, pp. 201–216; Electrolytic Dissociation, pp. 217–233; Balanced Actions, pp. 234–253; Rate of Chemical Transformation, pp. 254–265; Relative Strengths of Acids and Bases, pp. 266–282; Equilibrium between Electrolytes, pp. 283–295; Applications of the Dissociation Theory, pp. 296–310; Thermodynamical Proofs, pp. 311–332.

The general treatment is non-mathematical, a few thermodynamical proofs in the last chapter being the only exceptions. The book really includes nearly all the important topics usually taught in classes in physical chemistry. The absence of a chapter on photochemistry may be noted, as may also the treatment of Nernst's theory of the E. M. F. of galvanic cells. The

order in which the subjects are considered is different from the usual one. Without going into details concerning this point, it may suffice to say that the manner in which the separate chapters are written is such as to weave them together in a logical way. The author seeks to have the student connect physical chemistry with his previous chemical knowledge so as to make the new subject of real use to him.

Clearness of statement characterizes the book throughout. The relative amount of space devoted to some of the subjects is perhaps open to some criticism; so, for example, the subject of thermal chemistry is treated in ten pages. The author, however, does not intend this to suffice but directs the student to the treatise of Muir and Wilson on this subject.

In the discussion of the applications of the dissociation theory the author has wisely chosen to content himself almost entirely with a merely qualitative treatment, since the quantitative side of this subject (especially whenever it involves the combination of the law of mass action and the theory of electrolytic dissociation) leaves much to be desired.

The book is indeed an introduction to the study of physical chemistry, for a perusal of its pages will give the student a knowledge of general, fundamental facts and will lead him to further inquiry. The author is clearly not one of those who believe that the subject of physical chemistry is already in a high state of perfection and that there is but little left to do except to fill in the details. It is to be regretted that the book does not contain more references to original articles.

LOUIS KAHLENBERG.

WATER AND WATER SUPPLIES. By DR. JOHN C. THRESH. Second revised edition. vii+438. pp. Philadelphia: P. Blakiston's Son & Co. 1900.

Although this is called the second, revised edition of this work, it is an exact reproduction of the 1896 English edition, the only revision apparent being the correction of typographical and other errors in the first edition. It is nevertheless, a convenient handbook on water supplies.

The first part of the book treats of water, its composition, properties, etc.; the various sources of water supplies, as rain, surface, subsoil, spring, deep-well, and river water; the amount

and character of the water derived from these various sources; the nature and source of the impurities that may gain access to these different waters; and analyses of water supplies derived from these various sources. Then follow several chapters on the quality of drinking-waters; the effects upon health of impure waters; the interpretation of water analyses; the pollution of drinking-water; the self-purification of rivers. The purification of water, both on the large scale and for domestic purposes is treated of in subsequent chapters.

There is also a chapter on the laws relating to water supplies as comprised in the different special acts of Parliament with reference to the powers of individuals, towns and water companies, and likewise the various restrictions which have been raised in order to maintain the purity of natural water supplies.

The information contained in the book is drawn from the large personal experience of the author and from the voluminous literature on the subject. In this respect the author has shown considerable appreciation of the experiences of American investigators, especially the pioneer work performed in the study of filtration of water and sewage by the Massachusetts State Board of Health.

In discussing the interpretation of water analyses the author states that "Although a mere analysis cannot guarantee us purity and safety, yet it very frequently can reveal to us impurity and risk. When the source of a water, upon most careful examination by an expert, is found to be free from all danger of pollution, and the chemical examination proves that the inorganic constituents are unobjectionable, both in quantity and quality, and that organic matter is absent or present in barely appreciable amount, then safety, so far as human foresight can be trusted, may be guaranteed . . . . Chemical analysis, therefore, has its use; it is only when it is made the sole arbiter between safety and risk that it is abused, and is liable to lead to errors fraught with most disastrous consequences. Let the analysis be as careful and complete as possible, but let the results always be interpreted in the light afforded by a searching examination of the source of the sample."

At the close of the chapter he says: "Bacteriological, microscopical, and chemical examinations must always be associated

with a thorough investigation of the source of the water, to ascertain the possibility of contamination, continuous or intermittent. Then, and then only, if everything be satisfactory, we may be justified in speaking of safety and of freedom from risk; but where either bacteriological, microscopical, or chemical examination is unsatisfactory, the inquiry into the history of the water must be most careful and complete, and a guardedly-expressed opinion given only after a full consideration of the bearing of the one upon the other."

It is gratifying to read such positive statements with regard to the analysis of water for sanitary purposes because it is too frequently the case that either the chemist, bacteriologist, or the microscopist, or each of these, places undue value upon his results. Quite frequently all three forms of examination are necessary to form a definite idea as to the relative purity of a water. The author's long experience as an analyst and medical officer of health renders his opinion in this respect all the more valuable.

D. H. BERGEY.

A TREATISE ON CRYSTALLOGRAPHY. By W. J. LEWIS, M.A., Professor of Mineralogy in the University of Cambridge. Cambridge University Press. 8mo. 604 pp. Price, 14 shillings, net.

This is one of the most pretentious treatises on this subject which has appeared in the English language. The important, and, from a crystallographic standpoint, historic chair which the writer holds, has naturally given to his work a decidedly conservative tone, from which many modern students will differ.

There are ten chapters (140 pages) dealing with the general geometric properties of crystals; seven chapters (300 pages) on the different systems; one chapter (100 pages) on twin crystals; and two short chapters on "divers notations" and goniometers, respectively.

The chapter on the formation of crystals is fragmentary and altogether too brief. The same is to be said of the chapter on "the law of constancy of angle." "Symmetry" is introduced clumsily but illustrated satisfactorily. The chapter on "axial representation" is somewhat labored; many of the points could have been just as satisfactorily proved by less cumbersome geometrical proof. The heavy Euclidean methods are tedious. The chapter on zone-indices and relations of zones is well stated, and,

didactically, is perhaps the best chapter in the book; the chapter on the "anharmonic ratio" is also well done. Two chapters on crystal drawings and projections are satisfactory except for some more roundabout proofs, and the omission of all reference to gnomonic projection—an omission much to be deplored, for a projection which shows all zones as straight lines, instead of great circles, is surely worthy of the crystallographer's best attention.

The chapter on "The Systems" is unphilosophically written and, from a non-English point of view, indefensible. No attempt is made to explain clearly the philosophy of the matter. No clear proof is given why only 32 classes of forms (Groth's) are possible, and no satisfactory explanation of the peculiarities of the systems is attempted. The fact that Dr. V. Goldschmidt[1] has *proved* the unscientific nature of Groth's classification, and that the optical, thermal, electric as well as geometric properties of crystals all point to the six commonly accepted systems as the bases, the units, the fundamentals of crystal classification,—all this is overlooked. The old notion of making rhombohedral crystals into a seventh system is revived, although none of the physical properties of such crystals differentiate them from the hexagonal system; and further yet, Miller's axes of reference are retained instead of substituting the Bravais, which are universally conceded as better and more logical. This is one of the worst examples of unwise conservatism in the book.

The seven chapters on the systems are thoroughly and conscientiously worked out. Particularly praiseworthy are the large number of actual specimens described as examples, most of these being descriptions of crystals in the Cambridge Museum. The concrete examples thus furnished are a great help to understanding the text, besides being valuable crystallographic data in themselves.

The long chapter on twinning is lucidly written, and enriched by drawings and data concerning many interesting specimens from the Cambridge collections. It is the best chapter in the book.

Taken altogether, it is a good exposition of old-school crystallography, with the addition of Groth's classification, rather unskilfully presented. The details of crystal forms, calculations,

[1] *Ztschr. Krys.*, January, 1899.

twins, etc., are well done, and the book is chiefly valuable to the advanced student for this information. For beginners, or as an introduction to the main principles of crystallography, it is unsuited, for it is not sufficiently didactic in tone nor clear in presentation, while making the primary error of misconceiving the fundamentals of crystal classification.

The paper, type and drawings are first class, the binding rather frail, and the uncut edges an abomination.

JOSEPH W. RICHARDS.

BEGINSELEN DER SCHEIKUNDE. Door M. C. SCHUYTEN. Antwerpen. 1889. pp. 110. 8 vo.

The author of this little volume, who is professor at the Institute for Higher Studies in Brussels, as well as at the Technical School of Antwerp, has prepared for elementary classes a book on the rudiments of inorganic chemistry including chemical analysis. Naturally, in so small a compass some topics have to be treated superficially; thus spectrum analysis is dealt with in one page and three lines; half a page is given to the properties useful in determining minerals, and this is followed by a table giving the names, composition and chief properties of 84 minerals.

In the preface the author explains that he has adopted the sound principle to "go from the known to the unknown." The book is excellently printed, a variety of types assisting comprehension. The few illustrations are sectional. Questions are introduced to aid teacher and pupil.

H. C. B.

THE KINETIC THEORY OF GASES. Elementary Treatise with Mathematical Appendices. BY OSKAR EMIL MEYER. Translated from the second revised edition by ROBERT E. BAYNES. London, New York, and Bombay: Longmans, Green, & Co. 1899. xvi + 472 pp. 8vo. Cloth. Price, 15 shillings.

The first German edition of this treatise appeared in 1877, the first half of the second edition in 1895, and the second half in 1899. We have in the book before us the translation of the complete second edition.

In this revised edition the general plan of the first edition has been followed. The book is divided into three parts, together with six mathematical appendices. The subjects treated are as

follows: Part I. Molecular Motion and Its Energy, pp. 3–145; Part II. The Molecular Free Paths and the Phenomena Conditioned by Them, pp. 149–296; Part III. On the Direct Properties of the Molecules, pp. 299–352. The mathematical discussions connected with the treatment of these subjects are contained in the Appendices, pp. 355–466; they make no claim to completeness. While the contents of the book are limited to the same general range of phenomena considered in the first edition, an explanation on the kinetic theory of the resistance of air and of the reaction of a jet, together with an investigation concerning the influence of the dissociation of the molecules of a vapor upon its viscosity, have been inserted.

The author deserves much credit for the manner in which he has worked up the bulky literature of the subject which has accumulated during the past two decades. The translator has provided the English speaking public with a good translation of this valuable work. He has not added anything new except a few foot-notes, but he has provided an index that is an exceedingly valuable addition to the book.

Of late, criticisms of the kinetic theory of gases have frequently been heard, and it has even been charged that the theory has outgrown its usefulness and that it has done more harm than good. Nevertheless these very critics still gladly reach out for the kinetic theory whenever it can be used to explain some of their own pet theories, particularly those relating to the analogy between gases and solutions.

English-speaking scientists, and chemists in particular, will welcome this new English edition of Professor Meyer's excellent book.

The work of the publishers is very commendable.

LOUIS KAHLENBERG.

LABORATORY MANUAL. EXPERIMENTS TO ILLUSTRATE THE ELEMENTARY PRINCIPLES OF CHEMISTRY. BY H. W. HILLYER, PH.D., Assistant Professor of Organic Chemistry in the University of Wisconsin. 200 pp. New York: The Macmillan Co. 1899. Price $1.90.

The "book is written for the use of college students of general chemistry." The first and much the larger portion of the book, (Part I.) is devoted to the preparation and properties of the elements and their compounds; another portion (Part II;) presents a limited number of quantitative experiments for the

verification of quantitative laws: the appendix contains needful data for the students' use. In the selection of experiments the author provides for beginners, for those possessing slight familiarity with the subject, and for those who have had a satisfactory laboratory course in the preparatory school. The experiments are well chosen and graded, the directions are carefully stated, and the questions are plainly those of a painstaking teacher. The directions to the student regarding his preliminary preparation for each laboratory exercise are, in particular, excellent. The book is well printed and excellently bound.

H. P. TALBOT.

VOLUMETRIC ANALYSIS, SPECIALLY ADAPTED TO THE REQUIREMENTS OF STUDENTS ENTERING FOR THE ADVANCED PRACTICAL CHEMISTRY EXAMINATIONS OF THE SCIENCE AND ART DEPARTMENT. By JOHN B. COPPOCK. London: Whittaker & Co.; New York: Macmillan & Co. 12mo. pp. 92. Price, 50 cents.

The nature of this book is sufficiently indicated in the title. There is nothing contained in it worthy of special mention. It is chiefly notable for its omissions. Such books are of little value except to those who wish to pass an examination and have no further interest in the subject.

E. H.

BOOKS RECEIVED.

Leitfaden für den Unterricht in der anorganischen Chemie. Didaktisch bearbeitet von Dr. Joachim Sperber. Erster Teil. Zürick: Verlag von E. Speidel. 1899. 120 pp. Preis, M 2.40.

A Description of Some Chinese Vegetable Food Materials and their Nutritive and Economic Value. By Walter C. Blasdale. Bulletin No. 68, U. S. Department of Agriculture, Washington, D. C. 1899. 48 pp.

Preservatives in Canned Foods. Bulletin No. 165. 8 pp. Butter Adulteration. Bulletin No. 166. 12 pp. The North Carolina College of Agricultural and Mechanical Arts, Raleigh, N. C. 1899.

A Treatise on Crystallography. By W. J. Lewis, M.A. Cambridge: At the University Press. 1899. xii+612 pp. Price, 14 shillings net.

The Urine; and Clinical Chemistry of the Gastric Contents, the Common Poisons, and Milk. By J. W. Holland, M.D. Sixth Edition, Revised and Enlarged. Philadelphia: P. Blakiston's Son & Co. 1899. vii +124 pp. Price, $1.00.

Index to the Literature of Zirconium. By A. C. Langmuir and Charles Baskerville. City of Washington: Published by the Smithsonian Institution. 1899. 8vo. 29 pp.

The Chemistry of Essential Oils and Artificial Perfumes. By Ernest J. Parry. London: Scott, Greenwood & Co.; New York: D. Van Nostrand Co. 1899. viii+411 pp. Price, $5.00.

A System of Instruction in Qualitative Chemical Analysis. By Arthur H. Elliott and George A. Ferguson. Third Edition. 1899. Published by the Authors. 115–119 W. 68th St., N. Y. City. 155 pp. Price, $1.50.

Traité de la Fabrication des Liqueurs et de la Distillation des Alcools. Par P. Duplais, ainé. Septième édition, entiérement refendue par Marcel Arpin et Ernest Portier. Tome Premier—Les Alcools. 613 pp. 8 fr. Tome Second. Les Liqueurs. 606 pp. 10 fr. 1900. Paris: Gauthier-Villars. Quai des Grands-Augustins, 55.

The Cost of Living as Modified by Sanitary Science. By Ellen H. Richards. New York: John Wiley & Sons. 1899. 121 pp.

Beginselen der Scheikunde. Door Dr. M. C. Schuyter. Antwerpen: Jos. Ishoven, Van Straelenstraat, 8. 1899. 109 pp. Price, $1.50.

Agricultural Experiment Station of the University of Minnesota. Bulletin No. 63.—Miscellaneous Analyses, Composition of Tomatoes, Proteids of Wheat Flour. 50 pp. Bulletin No. 65.—Soil Investigation. 84 pp. 1899. St. Anthony Park, Minn.

The North Carolina Agricultural Experiment Station, Twenty-second Annual Report; Bulletin No. 152–163. Contents.—Reports of officials; poultry notes; vinegar adulteration; the adulteration of coffee and tea; baking powders; the adulteration of flour; mineraline; the fertilizer control for 1898; horticultural experiments during 1896; digestive experiments; drinking water; farming in North Carolina; rational stock feeding; the flora of North Carolina; preservatives in canned foods; butter; poultry experiments; field and forage experiments; feeding experiments and milk records. lii+462 pp. Raleigh, N. C.

Lexikon der Kohlenstoff-Verbindungen. Von M. M. Richter. Zweite Auflage der "Tabellen der Kohlenstoff-Verbindungen nach deren empirischer Zusammensetzung geordnet." Thirty parts. 2000 pp. Price, M. 1.80, per part.

Petroleum Series—Bulletin No. 3. The School of Mines, University of Wyoming, Laramie, Wyoming. 32 pp.

Water and Water Supplies. By John C. Thresh. Second revised edition. Philadelphia: P. Blakiston's Son & Co. 1900. xv+438 pp. Price, $2.00.

Baking Powders. A treatise on the character, methods for the determination of the values, etc., with special reference to recent improvements in phosphate powders. By Charles A. Catlin. Published by the Rumford Chemical Works, Providence, R. I. 1899. 44 pp.

Water and Water Supplies. By John C. Thresh. Second revised edition. Philadelphia: P. Blakiston's Son & Co. 1900. xv+438 pp. Price, $2.00.

Annuaire pour l'An 1900, publié par le Bureau des Longitudes. Avec des Notices scientifiques. 628 pp. Les Machines Génératrics de Courants Électriques. Par M. A. Cornu. 89 pp. Les nouveaux Gaz de l'Atmosphere. Par M. G. Lippmann. 15 pp. Les Travaux au Mont Blanc en 1899. Par M. J. Janssen. Sur l'Application de l'Aéronautique. Par M. J. Janssen. 2 pp. Discours prononcés a l'Inauguration de la Statue de Félix Tisseraud. 19 pp. Liste des Membres qui Composent le Bureau des Longitudes. 37 pp. Paris: Gauthier-Villars, quai des Grands-Augustins, 55. In one volume. Price, 1 fr. 50 c.

The Kinetic Theory of Gases. Elementary treatise with mathematical appendices. By Dr. Oskar Emil Meyer. Translated from the second revised edition by Robert E. Baynes. New York: Longmans, Green & Co. 1899. xvi + 472 pp. $4.00.

Elementary Chemistry for High Schools and Academies. By Albert L. Arey, C. E. New York: The Macmillan Co. 1899. xi + 271 pp. Price, 90 cents.

Introduction to Physical Chemistry. By James S. Walker, D.Sc., Ph.D. London & New York: The Macmillan Co. 1899. x + 335 pp. Price, $2.50.

Fifth Annual Report of the Montana Agricultural Experiment Station (Bulletin No. 20). 34 pp. Sheep Feeding (Bulletin No. 2). 13 pp. Agricultural Experiment Station, Bozeman, Montana.

Optical Activity and Chemical Composition. By Dr. H. Landolt, Professor of Chemistry in the University of Berlin. Translated with the Author's permission by John McCrae, Ph.D. New York: The Macmillan Co. 1899. xi + 158 pp.

Dietary Studies of Negroes in Eastern Virginia in 1897 and 1898. By H. B. Frissell and Isabel Bevier. Bulletin No. 71, U. S. Department of Agriculture, Washington, D. C.

The Theory of Electrolytic Dissociation and Some of its Applications. By Harry C. Jones, Associate in Physical Chemistry in Johns Hopkins University. New York: The Macmillan Company. 1900. xii + 289 pp. Price, $1.60.

The Slate Belt of Eastern New York and Western Vermont. By T. Nelson Dale. Extract from the Nineteenth Annual Report of the Survey, 1897-98. Part III.—Economic Geology. Washington: Government Printing Office. 1899. 155 pp.

Sheep Feeding. By J. H. Stewart and Horace Atwood. Bulletin No. 61. West Virginia Agricultural Experiment Station, Morgantown, W. Va. 12 pp.

A Study of the Effect of Incandescent Gas-light on Plant Growth. By L. C. Corbett. West Virginia Agricultural Experiment Station, Morgantown, W. Va. 24 pp., with numerous plates.

Commercial Feeding Stuffs in the Connecticut Market. Connecticut

Agricultural Experiment Station, New Haven, Conn. Bulletin No. 130, January, 1900. 40 pp.

Twenty-third Annual Report of the Connecticut Agricultural Experiment Station for 1899. Part I.—Fertilizers. New Haven, Conn. 92 pp.

Victor von Richter's Organic Chemistry or Chemistry of the Carbon Compounds. Edited by Prof. R. Anschütz (assisted by Dr. G. Schroeter). Authorized translation by Edgar F. Smith, Professor of Chemistry, University of Pennsylvania. Third American, from the Eighth German Edition. Volume II.—Carbocyclic and Heterocyclic Series. Philadelphia: P. Blakiston's Son & Co. 1900. xvi + 671 pp. Price, $3.00.

The Elms and Their Diseases.—Bulletin No. 84. 25 pp. with plates. Commercial Fertilizers.—Bulletin No. 85. 53 pp. Kentucky Agricultural Experiment Station, Lexington, Ky.

Annuaire de l'Observatoire Muncipal de Paris, dit Observatoire de Montsouris, pour l'Année 1900. (Analyse et Travaux de 1898.) Meteorologie—Chemie—Micrographie. Applications a l'Hygiene. Paris: Gauthier-Villars. xii + 578 pp. Price, 2 fr.

A Pocket-book for Chemists, Chemical Manufacturers, Metallurgists, Dyers, Distillers, Brewers, Sugar Refiners, Photographers, Students, etc. By Thomas Bayley. Seventh Edition, revised and enlarged. London: E. & F. N. Spon; New York: Spon & Chamberlain. 1900. 559 pp. Price, $2.00.

Volumetric Analysis. Specially adapted to the requirements of students entering for the advanced practical chemistry examinations of the science and art department; also the intermediate science and preliminary scientific examinations of the University of London. By John B. Coppock, F.C.S., Inter. B.Sc. (Lond.). London: Whittaker & Co.; New York: The Macmillan Co. 1899. 92 pp. Price, 50 cents.

Analyses of Commercial Fertilizers and Paris Green. Bulletin of the Agricultural Experiment Station of the Louisiana State University and A. & M. College, Second Series, No. 58. 90 pp.

The Work of the Agricultural Experiment Stations on Tobacco. Abstracted by J. I. Schulte, with introduction and comments by Milton Whitney. U. S. Department of Agriculture, Report No. 63. Washington, D. C. 1900. 48 pp.

ERRATUM.

In the number for February, 1900, p. 139 line 10, for "$[(CH_3)_2NH]_2TeCl_4$" read "$[(CH_3)_2NH]\ TeCl_6$."